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THE UNIVERSITY OF CHICAGO

A THESIS

SUBMITTED TO THE FACULTY OF DIVINITY OF CHICAGO  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF THEOLOGY

BY

EDMUND A. BURKE  
AUGUST, 1944







Thesis  
1964(F)  
#19D

THE UNIVERSITY OF ALBERTA

"THE RADIOLYSIS OF ETHANOL"

by

JAMES J. J. MYRON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA  
AUGUST, 1964







ABSTRACT

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "The Radiolysis of Ethanol" submitted by JAMES J. J. MYRON in partial fulfilment of the requirements for the degree of Doctor of Philosophy.







## ABSTRACT

The  $\gamma$ -radiolysis of ethanol has been investigated with particular reference to the main products hydrogen, acetaldehyde and 2,3-butanediol. Three different processes for hydrogen formation involving solvated electrons, hydrogen atoms and unscavengeable precursors are operative. A mechanism involving ionic species is presented to account for the main products of the radiolysis. The electron precursor of hydrogen is the most sensitive to impurities and gives hydrogen only at low doses ( $< 1 \times 10^{20}$  e.v./gm.). The hydrogen atom precursor can be affected by additives (benzene and 1,3-pentadiene were used). Such studies allowed an estimation of G(hydrogen atoms) in the system to be made. These inhibitor experiments pointed out the occurrence of processes that did not involve scavengeable entities.

Yields of minor products were also measured to complement the radiolysis study. An experimental mass balance between G(H<sub>2</sub>O) and G(products involving C<sub>2</sub> hydrocarbon fragments) was obtained. The importance of a secondary reaction of acetaldehyde in the determination is discussed.

Gas phase experiments were carried out to determine the effect of phase on product distribution. Deuterated ethanol radiolysis showed that both the CH<sub>2</sub> and the OH positions in the molecule are important for hydrogen production while the methyl





group is of secondary importance. The effect of hydrogen bonding on hydrogen production is also demonstrated by these studies.





## ACKNOWLEDGEMENTS

The author wishes to acknowledge the guidance and interest received from his research director, Dr. G. R. Freeman.

The patience and understanding of the author's wife, Maude, is also deeply appreciated by him.

Acknowledgement of the fine co-operation and able assistance of the Chemistry Department technical staff is also gratefully given.

The author also wishes to thank Mrs. Gail Conway and Mrs. Judith Abbott for typing the thesis.





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## INTRODUCTION

### (A) Historical Background.

From the time that ionizing raditions were discovered by Roentgen and Becquerel at the turn of the century, until the 1940's, a relatively small number of researchers were active in the field of radiation chemistry. S. C. Lind and W. A. Mund were among the prominent names connected with radiation chemistry during the early years. These workers mainly concentrated their efforts on the investigation of the radiolysis of simple chemical compounds in the vapor state. Alpha particles were commonly employed as the radiolytic agent, due to their comparatively high absorption in these media.

However, with the advent of nuclear fission "piles" certain areas of radiation chemistry immediately assumed considerable practical importance. In order to design efficient and economical units to produce usable power from nuclear fission it was necessary to study the effect of the very intense bombardment of high energy radiations on pile coolants, moderators, structural materials, lubricants etc. As heavy water was (and is) a popular moderator and coolant, the radiolysis of light and heavy water naturally attracted much study, a fact which is attested to by the number of publications dealing with this presumably simple, but factually complex system.

While the radiation chemistry of water was developing, the study of the radiolysis of other chemical compounds was also being undertaken. Some compounds were studied because of their direct potential use as components of an atomic pile, while others were investigated, hopefully, to





elucidate the behavior of related chemical compounds (used in atomic pile construction) upon irradiation.

Hence, the impetus for the present development of radiation chemistry arose from nuclear pile technology. Moreover, its study is also of great importance due to the biological factors involved.

On the one hand, it may be stated that the study of radiation chemistry is in its infancy and hence it cannot be expected that it should, at present, be based on firm, clearly understood principles that allow quantitative treatment leading to extrapolation to systems not yet studied. On the other hand, such a large volume of published data has been accumulated that one might expect that the detailed interaction mechanism of radiation and simple chemical compounds would be well understood. Unfortunately, in common with other branches of kinetic study, such is not the case. Even (and perhaps especially) the radiolysis of water is still the object of much speculation and proposed theory, which attempts to explain and correlate the mountains of data available on the subject. Two distinct and opposed fields of thought, arising from the views of Platzman<sup>(1)</sup> on the one hand and Samuel and Magee<sup>(2)</sup> on the other, leave the detailed mechanism of formation of the solvated electron indeterminate to this day. It is therefore perhaps not too surprising that the radiolysis mechanisms of organic compounds are also not clearly established.

The aim of this thesis is to provide new data for the  $\gamma$ -radiolysis of ethyl alcohol and to use these data to speculate on the radiolytic decomposition mechanism.



(B) Physical Aspects of  $\gamma$ -Ray Absorption by Matter.

Cobalt<sup>60</sup>  $\gamma$ -rays were used exclusively in this investigation.

Therefore, it is pertinent to outline the mode of  $\gamma$ -ray absorption by matter.

Gamma rays are electromagnetic radiation of short wavelength arising from a nuclear transformation within an atom. The decay of a Co<sup>60</sup> nucleus results in the production of two  $\gamma$ -rays and one  $\beta$ -particle. This  $\beta$ -particle which has an energy of 0.3 Mev (million electron volts) cannot penetrate the glass walls of a sample container and hence cannot effect chemical changes in a sample. The two  $\gamma$ -rays have energies of 1.17 and 1.33 Mev. These energies are close enough to each other that Co<sup>60</sup> is said to emit  $\gamma$ -rays of 1.25 Mev.

Gamma rays lose energy to a medium through which they pass by five different processes; a) Photoelectric absorption b) Pair production c) Coherent scattering d) Photonuclear reactions e) Compton scattering<sup>(3)</sup>.

In the photoelectric absorption process an atom of the medium absorbs the  $\gamma$ -ray; this results in the ejection of an orbital electron. This electron acquires the total energy of the incident ray minus the binding energy. Photoelectric absorption is most probable for atoms of high atomic number and for low photon energies. It can be neglected for the interaction of Co<sup>60</sup>  $\gamma$ -rays with materials composed of carbon, hydrogen, oxygen and the other low atomic number elements.

Pair production results in a positron-electron pair. The rest mass of these two particles has the energy equivalent of 0.51 Mev each. Therefore, the incident photon must have an energy of at least 1.02 Mev before



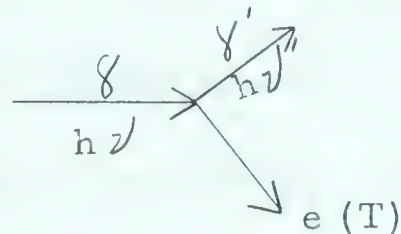


pair production is possible. The cross section per atom for this process is proportional to the square of the atomic number and it does not contribute significantly to energy absorption in samples of most organic molecules.

Photonuclear reactions require high energies ( $>10$  Mev) and are usually unimportant in radiation chemistry studies.

Coherent scattering of photons involves scattering resulting in small energy loss to the X or  $\gamma$ -ray. When the interaction is between atomic electrons and incident photons the process is called R<sup>x</sup>leigh scattering. Energy loss by this mode is important at low ( $<0.1$  Mev) energies and in materials composed of high atomic number elements.

Compton scattering occurs when the incident  $\gamma$ -ray transfers a part of its energy to an electron. Unlike photoelectric absorption the Compton process can take place with bound or free electrons.



The kinetic energy imparted to the electron (T) is given by <sup>(4)</sup>

$$T = h\nu - h\nu'$$

where  $h\nu$  is the energy of the incident photon

$h\nu'$  is the energy of the photon after "collision".

This equation ignores the small binding energy of a bound electron.

The Compton electronic absorption coefficient is independent of atomic number, and the process predominates over those mentioned above over a wide energy range. It is the only important way by which the energy of  $\text{Co}^{60}$   $\gamma$ -rays is lost in materials of low atomic number.



After production of the Compton electron, the photon of reduced energy normally passes through the system without further interaction. However, the high velocity electron can produce further ionization as well as excitation. Thus, the primary electron collides with another molecule of the medium, generating another ion pair whose electron in turn has sufficient energy to produce further ionization. These secondary charged particles, if they possess sufficient energy, in a similar fashion, give rise to more ionization and excitation so that the energy of the primary Compton electron is degraded in a series of successive steps until all the electrons have insufficient energy to effect further ionization. Even when electrons have fallen to such energies, they still may have the ability to excite orbital electrons of a molecule to a higher energy state. These excited molecules are chemically reactive species and the relative chemical importance of the ions and molecules produced in the above manner has been the subject of much controversy.

The fate of the electrons that have fallen to an energy below the lowest excitation energy of the medium is another matter that has been the subject of much speculation. Platzman<sup>(5)</sup> has pointed out that trace impurities having lower excitation potential than the main bulk of the medium could be excited through encounters with these "sub-excitation" electrons. It is possible that such a phenomenon is partly responsible for the fact that the degree of purity of a substrate often has marked influence upon the observed radiolytic yields.

Thus, the end result of the sequence of events outlined above is that the initial Compton electron has generated a great number of chemically





active species in the medium in which it was born.

It has been estimated that a 1 Mev electron may produce  $3 - 4 \times 10^4$  additional ionizations and  $5 - 8 \times 10^4$  excited molecules<sup>(6)</sup>. The entire process of generating these chemically reactive entities is complete  $\approx 10^{-15}$  (7) sec. after the initial interaction of the  $\gamma$ -ray with the medium.

Some characteristics of these intermediates and the processes by which they give rise to observed chemical changes will be discussed in the following section.

### (C) Chemical Consequences of Radiation Absorption.

#### a) Formation of Chemical Intermediates.

All chemical changes occur through transient states of higher than average energy<sup>(8)</sup>. The intermediates formed in the sequence of events mentioned above have special features peculiar to radiation chemistry. They occur in greater variety and at higher energy than in thermal or photochemical reactions. In condensed systems they are formed in unique geometrical patterns which impart special characteristics to radiolysis reactions.

This unusual spatial distribution of the reactive species is a direct result of the nature of energy absorption from ionizing radiations by matter. If we consider the path of a fast electron produced by a  $\text{Co}^{60}$   $\gamma$ -ray<sup>(9)</sup>, the vast majority of ionizations and excitations will be found close to the electron track. A number of reactive regions that are relatively well separated from each other will roughly outline the track. As the primary (Compton) electron and its associated lower energy secondary electrons are slowed down, the rate



at which they impart energy to the surrounding molecules becomes greater and the density of events increases correspondingly. Regions or packets of dense ionization and excitation are known as spurs. The diameter of a spur has been estimated to be approximately  $20 \text{ \AA}^{(10)}$ . The linear density of events along a track is termed "linear energy transfer" (LET) and is much greater for heavy multi-charged particles, such as  $\alpha$ -particles, compared to the electrons arising from  $\gamma$ -ray absorption. An  $\alpha$ -particle track is essentially the axis of a cylinder of ionization and excitation. This inhomogeneity of distribution has a marked effect upon the ensuing chemical reactions by facilitating radical-radical reactions and rendering scavengers less efficient than they would be if the scavengable species were distributed uniformly throughout the system.

b) Approximate Time Scale for Radiation Chemistry.

Various authors (7) (11) (12) have outlined time regions during which various processes occur in radiation chemistry. A summary of the general features of these time scales follows.

During the initial  $10^{-15}$  seconds the particle and the system interact and the spurs are formed. From  $10^{-15}$  seconds to  $10^{-12}$  seconds radicals are generated, "cage" reactions and ion-molecule reactions occur. After this period up to approximately  $10^{-7}$  seconds the spurs expand by diffusion of the reactive entities they contain. In the same time interval, reactions inside the spurs or tracks can take place. From  $10^{-7}$  seconds onwards processes in the bulk medium, such as the interaction of radicals with scavengers, occur.





c) The G-value.

The G-value is almost universally used by radiation chemists to calculate the extent of decomposition in a system.

$G(x) =$  the number of molecules of a compound  $x$  formed  
or destroyed per 100 e.v. absorbed by the system.

Unlike the quantum yield of photochemistry, the G-value has no direct theoretical significance but is employed as a matter of convenience.

(D) Radiolysis of Organic Compounds

a) General

The decomposition agent in radiolytic studies is usually of very high energy, the reactive intermediates are varied, and the possible reactions of these species are numerous. Therefore, it might be thought that complete randomness of decomposition is a feature of radiation chemistry. This is not the case.

Some degree of specificity of decomposition products has been observed in a number of systems<sup>(13-16)</sup>. Early investigators of the radiolysis of alcohols<sup>(17)(18)</sup> showed that, while a fairly large number of products were found, many of these were present in small amounts, and a large proportion of the decomposition could be accounted for, by consideration of a few major products. Indeed, with the advent of refined analytical techniques, employing high sensitivity gas chromatography, mass spectrometry, etc., many photochemical and thermal reactions are proving to be more complicated



than was originally thought.

b) Effect of Phase.

The proximity of excitation and ionization events that leads to high local concentrations of radicals<sup>(19)</sup> gives rise to "track effects" in liquids and solids. These may be unimportant if the radicals react easily with solvent. Then, changing LET would not affect product yields. However, LET does affect the product distribution in the radiolysis of liquid alcohols. In this connection, McDonell and Gordon<sup>(20)</sup> found a glycol/aldehyde ratio of 1 for  $\alpha$ -particle bombardment and a ratio of 2 for  $\gamma$ -ray bombardment of liquid methanol.

As the density of organic gases is some 2 or 3 orders of magnitude less than that of their liquids, track effects might be expected to be negligible in this phase. Comparison of  $\alpha$ -particle radiolysis data<sup>(21)</sup> with results obtained in the present investigation with  $\gamma$ -rays, indicates that this may not be so.

An important difference arising from the physical state during irradiation is the operation of a cage effect in condensed phases<sup>(22)</sup>. This phenomenon (termed the Franck-Rabinowitch effect) occurs when bond breakage results in relatively large radical fragments:



(R is an alkyl radical)

These fragments can be held in position by neighbouring molecules, so that they react with each other and, except for radical disproportionation,





no chemical change results. If a C-H bond ruptures, as appears to be common in aliphatic alcohols, the small size and large mobility of the hydrogen atom cause recombination to be much less likely. Gas phase radiolysis of alcohols should be essentially free of cage effects, due to the much lower phase density, while solid phase irradiations should exhibit this effect more strongly than liquids. The expected increase in the extent of decomposition (resulting from C-C bond breakage) on going from the solid to the liquid to the gas phase has been observed in the case of ethanol.<sup>(23)</sup> <sup>(21)</sup> The extent to which higher temperatures affect the increase, due to the inherent increase in energy of the molecules, is difficult to determine. However, Baxendale and Sedgewick<sup>(24)</sup> observed greater decomposition in gaseous methanol irradiated at room temperature, compared to that in the liquid<sup>(25)</sup> at the same temperature. Abrupt changes in yields from alcohols have also been demonstrated at the liquid to solid transition point<sup>(26)</sup> for aqueous alcohol solutions.

Irradiations at 77°K with glassy and crystalline solids indicate that glassy samples experience greater decomposition than do those present as crystals during irradiation<sup>(27)</sup>.

#### c) Effect of Dose Rate.

Variation of dose rate in some radiolytic systems has a marked effect upon product yields (e.g. radiation induced polymerization)<sup>(28)</sup>. The effect of varying the dose rate by factors of 10-100, for liquid aliphatic alcohols, seems to be small. Lichtin<sup>(29)</sup> irradiated liquid methanol with



Co<sup>60</sup>  $\gamma$ -rays (at a dose rate of  $1.8 \times 10^{16}$  e.v./ml.min) and 1.95 Mev Van de Graaf electrons (at a dose rate of  $3.7 \times 10^{18}$  e.v./ml.min.). The LET for both are approximately the same. Despite the 200 fold difference in dose rate the same relative yields of hydrogen, ethylene glycol and formaldehyde were obtained.

d) Effect of Total Dose.

The extent to which a sample has been radiolyzed has been found to affect the G values of products for alcohols. Hydrogen yields were found to vary with total dose for liquid methanol<sup>(29)</sup>. Newton and McDonell<sup>(30)</sup> found that the yields of the major products from liquid ethanol decreased to varying degrees with increasing dose.

e) Effect of Temperature.

When a system is elevated in temperature, the radiolytic primary processes should not be affected. Subsequent processes could show a temperature dependence if the radicals involved are thermalized before reacting<sup>(31)</sup>.

(E) Radiolysis of Alcohols.

a) General.

The most extensive investigation of the radiolysis of aliphatic alcohols was that of McDonell and Newton<sup>(17)</sup>. They employed 28 Mev helium ions to decompose ten liquid, air free alcohols ranging from methyl to n-decyl alcohol. Extensive product analysis by chemical means revealed





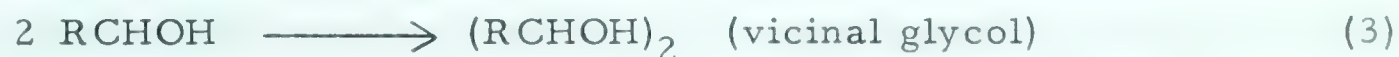
that hydrogen, unsaturated and saturated hydrocarbons, carbon monoxide, glycols, aldehydes, ketones, and water were present in significant quantities. Trace quantities of acid, peroxides, ethers and non-substrate alcohols were also detected in some instances.

Hydrogen was the main gaseous product from all primary and secondary alcohols. (Tertiary-butanol gave more methane than hydrogen). As the chain length of the alcohols increases,  $G(H_2)$  remains essentially constant, while the hydrocarbon, vicinal glycol and aldehyde yields decrease. This reflects a lowering of reactivity at the functional group as the long chain alcohols tend to react in the manner of hydrocarbons.

For the primary alcohols, glycol and aldehyde were the principal liquid products. The fact that the glycols were very predominantly vicinal glycols indicates that loss of a hydrogen atom from the  $\alpha$ -position of the alcohol is an important step at some stage in the radiolysis: e.g.



followed by



A possible source of at least part of the aldehyde could be the disproportionation of these radicals:



The nature of the products from all the alcohols suggested that groups attached to the carbinol carbon atom were the most sensitive to ionizing radiations. Hydrogen atoms were shown to be more susceptible to removal than were small alkyl groups attached to this carbon atom.



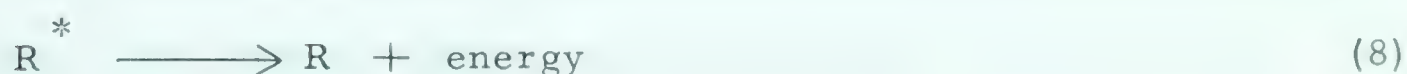
As water was a significant product in all cases, it appears that the C—O bond is also vulnerable. However, x-1 carbon hydrocarbons from x- carbon primary alcohols were present in greater yields than x- carbon hydrocarbons. The amounts of water that could be accounted for, from the associated hydrocarbon yields, are much less than  $G(H_2O)$  observed. Undetected products such as higher alcohols or polymer could explain the water discrepancy.

The lack of appreciable quantities of ethers and peroxides might reflect on the resistance to scission of the O—H bond. However, the instability of the simpler peroxides might be a factor contributing to their very low yields.

Another possibility is that any  $RCH_2O$  radicals, formed from O—H rupture, undergo an abstraction process involving the substrate, before the alkoxy radicals can give rise to characteristic products



The reactions mentioned above do not take into account any role of ions. This would seem to indicate that ions are neutralized before they can enter into product forming reactions. i.e.

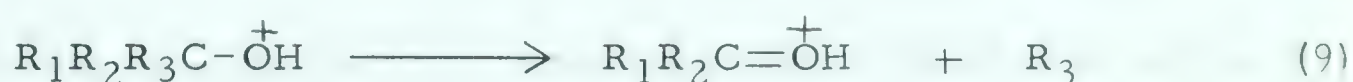


Williams<sup>(32) (33)</sup> has theorized that parent ion-molecule reactions can precede the neutralization process in both the liquid and gaseous phases. On energetic grounds, it seems likely that the electron removed to form the





parent ion in alcohols is one of the non bonding electrons of the oxygen atom. Cummings and Bleakney<sup>(34)</sup> proposed that this type of ionization tended to promote "trivalent oxygen". Thus, oxygen is inclined to form an additional bond with its neighbouring carbon atom. This disposition for  $\text{>C}=\overset{+}{\text{O}}\text{-H}$  formation would be favored by loss of a hydrogen atom or alkyl group from the carbinol carbon atom.



followed by



A second path by which the ionized oxygen can complete its valence shell of electrons is through hydrogen atom abstraction<sup>(33)</sup> from a neighbouring molecule



and then



or



followed by



Thus the apparent chief radical intermediates for alcohol radio-lysis can arise from primary processes involving ions. This picture is also consistent with the reactivity of groups attached to the carbinol carbon atom.

Ion-molecule reactions are thought to have little or no activation



energy<sup>(35)</sup> and are considered frequently to occur at every encounter<sup>(36)</sup>.

Reactions of this type involving alcohols have been directly observed in the mass spectrometer<sup>(37-40)</sup>.

The reaction



has been found to proceed faster than similar reactions involving hydrocarbons.

The specific reaction rate for (14) is approximately 10 times as fast as



It is possible that an ion-molecule reaction of ethanol analogous to (14) plays a significant role in hydrogen formation through a reaction involving  $\text{CH}_3\text{CH}_2\dot{\text{O}}\text{H}_2$ <sup>(21)</sup>.



If the above, and similar, reactions were important in ethanol radiolysis, comparison of data from studies of various deuterated ethanols irradiated in the liquid and gaseous phases should prove fruitful. In the vapor phase any intermolecular structure arising from hydrogen bonding would be absent. Isotope analysis of the radiolytic hydrogen could support or militate against any hypothesis regarding this type of reaction.

In the following section some comments will be made concerning past studies of the radiolysis of alcohols.

## b) Ethanol.

### (i) Bond Strengths.

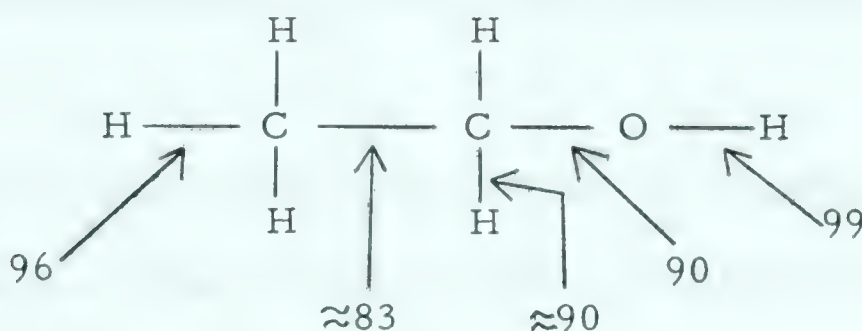
Chemical reactions need not proceed exclusively via modes





influenced by bond strengths in a molecule. Nevertheless, some attention should be paid to relative bond dissociation energies, especially if reaction occurs through intermediates that are thermalized with respect to the medium.

Bond dissociation energies, in kcal/mole, for the various bonds in the ethanol molecule are given below.



The figures quoted above were obtained as follows. The C—O and O—H bond values are by Gray<sup>(41)</sup>. The C—H value for the methyl group was assumed to be that quoted for ethane by Cottrell<sup>(42)</sup>, who also cites a 6 kcal difference in dissociation energy for the primary and secondary C—H bonds in propane. Hence, the approximate value of 90 kcal for the C—H bond in the CH<sub>2</sub> position in ethanol is given. The C—C bond strength is that quoted for ethane<sup>(42)</sup>. The figures, while approximate, indicate that the C—C bond is the weakest bond in the molecule. Of the three types of bonds to hydrogen atoms, the C—H bond of the  $\alpha$ -position appears to be the weakest.

#### (ii) Radiolysis Studies.

There is considerable discrepancy between the  $G(\text{H}_2)$  values for liquid ethanol reported in the literature. The values have ranged from 3.5 to 5.5<sup>(17)(23)(30)(43)(44)</sup>. This may, in part at least, be due to different experimental conditions (such as dose rate, total dose, type of ionizing radiation etc.). A second source of the variation could be the presence of



small amounts of impurities, that may function as protectors or scavengers. The results could be markedly affected, depending upon the nature and quantity of these foreign materials. In this connection, Newton and McDonell<sup>(30)</sup> found that the addition of small amounts of hexene-1 or acetaldehyde reduced the yield of hydrogen considerably. Recent work has shown that added acid increases  $G(H_2)$  over that observed in pure liquid ethanol<sup>(45)</sup>.

There are two points of speculation relating to hydrogen formation from ethanol. The first question is, to what extent do radical and "molecular" reactions occur. The second deals with the relative importance of the three kinds of hydrogen atoms in the ethanol molecule for hydrogen production. Added scavengers should be helpful in the first regard, while isotopic alcohols have shed light on the latter question.

In a study with hydrogen atom and methyl radical scavengers<sup>(25)</sup>, it was found that approximately 40% of the hydrogen (termed "molecular hydrogen") arose from processes that were not affected by the scavengers. Some 25% of the methane was designated "molecular methane". Such processes could involve hot atom reactions with ethanol or spur reactions. This type of study may be influenced by the efficiency of the inhibitor or protector used. Thus, it has been shown that cyclohexene is more efficient than benzene in reducing  $G(H_2)$  obtained by gas phase radiolysis of ethanol<sup>(46)</sup>.

Pulse radiolysis studies by Dorfman<sup>(47)</sup> gave a reactive intermediate with a UV absorption band that was attributed to  $CH_3CHOH$ . This radical could possibly result from an ethoxy radical precursor. The yield





of the solvated electron in ethanol was found to be  $1.0 \pm 0.3^{(48)}$  and it is thought that it is a precursor of part of the radiolytically formed hydrogen. Support for this hypothesis is the observation of Hayon and Weiss<sup>(43)</sup> that electron acceptors decrease  $G(H_2)$  from ethanol.

Various studies of irradiated alcohols in the solid phase have indicated the nature of some of the reactive intermediates present in the systems. Solid ethanol becomes colored when irradiated at low temperatures (27). Electron spin resonance (ESR) shows the presence of  $CH_3CHOH^{(49)}$ . An underlying ESR spectrum increases when the color centres are bleached indicating that the colored species is a precursor to part of the paramagnetic spectrum<sup>(50)</sup>. The precursor could be the ethanol ion<sup>(27)</sup>. Hydrogen atoms were not detected. The paramagnetic species can be stored at  $-196^\circ C$  indefinitely.

Johnsen<sup>(23)(51)(53)</sup> exposed  $\gamma$ -irradiated alcohols at  $-190^\circ C$  to visible and ultra-violet light. With visible bleach and subsequent warming, somewhat increased yields of hydrogen, methane, and carbon monoxide were observed for the lower alcohols. Dramatic increases in gaseous products, compared to samples thawed in the dark, resulted from bleaching with ultra-violet light. For ethanol the increase ratio for hydrogen was 8, for methane it was 40, and for carbon monoxide it was 900. These enhanced yields were attributed to photolysis of alcohol radicals



followed by





Double arrows are used as some reversibility of the photolysis was indicated by annealing experiments.

On going from the solid to the liquid state (no photolysis)  $G(2,3\text{-butanediol})$  increased while  $G(\text{acetaldehyde})$  decreased.

If, in the UV bleaching experiments, all the alcohol radicals were photolyzed, one might expect to find no acetaldehyde and more probably no 2,3-butanediol after bleaching. Nevertheless, appreciable quantities of both were found.

Electron spin resonance studies of ethanol could not distinguish between  $\text{CH}_3\text{CHOH}$  and  $\text{C}_2\text{H}_4^+$  <sup>(53)(54)</sup>. Thus, for some time the second species had to be considered as being possibly responsible for the ESR quintet observed in ethanol in the solid phase.

However, Johnsen could correlate the observed carbon monoxide yields (after bleaching) with values of  $G(\text{radicals})$  for ethanol and methanol reported by Alger et. al. <sup>(50)</sup>. As the UV absorption is associated with the paramagnetic spectrum <sup>(27)</sup>, (the ESR signal disappears when the sample is bleached by UV of suitable wavelength), the carbon monoxide results from the photolysis of the paramagnetic species. Since  $\text{C}_2\text{H}_4^+$  could not generate carbon monoxide, most, if not all, of the ethanol ESR quintet is due to  $\text{CH}_3\text{CHOH}$ . Similarly, the methanol triplet arises from  $\text{CH}_2\text{OH}$  and not  $\text{CH}_2^+$ .

#### c) Methanol.

Studies similar to, and in some cases, in conjunction with the ones



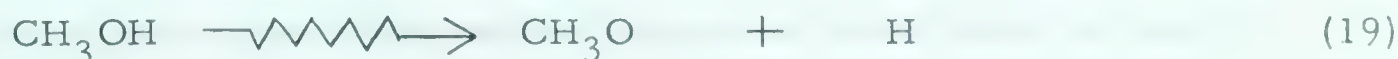


outlined above showed that the radiolysis of methanol has many features in common with that of ethanol. Unfortunately, the similarity extends to disagreements in yield values (including that for the main product hydrogen) (20)(55-58) reported by various workers. As in ethanol, the aldehyde/glycol ratio varies with conditions<sup>(20)</sup>.

There is evidence that hydrogen is produced by at least three processes: the first two involve electrons and hydrogen atoms, while the third mode is one that is unaffected by additives<sup>(58)</sup>. Lichtin<sup>(55)</sup> as well as Baxendale and Mellows<sup>(58)</sup> have demonstrated the effect of trace impurities and various purification techniques upon yields. Formaldehyde seems to be the major product that is least affected.

The possible role of ion-molecule reactions has been discussed by Theard and Burton<sup>(59)</sup>. The ions involved in such a process could be the result of a primary step involving the ionic species called "polarons" by Hayon and Weiss<sup>(60)</sup>.

There is little doubt that  $\text{CH}_2\text{OH}$  radicals are an important intermediate at some stage in the radiolysis. However, it has not been clearly established that they are the only important primary radical produced in quantity. The initial step



may occur to a considerable extent,  $\text{CH}_2\text{OH}$  radicals resulting from



Electron spin resonance observations<sup>(61)</sup>, combined with product yield measurements from UV bleached irradiated methanol<sup>(23)</sup> show the



presence of  $\text{CH}_2\text{OH}$  in solid methanol.

Scavenger studies indicate that appreciable fractions of the hydrogen and methane originate from processes involving non-scavengeable precursors. Benzene, while affecting  $G(\text{H}_2)$  considerably, did not affect  $G(\text{formaldehyde})$ .

Adams et al<sup>(62)</sup> have investigated the role of the solvated electron in the radiolysis. Using pulse radiolysis combined with flash spectroscopy, it was shown that an absorption with a maximum at  $\approx 6200 \text{ \AA}$ , attributed to the solvated electron, could be observed in basic methanol but not in neutral or acidic methanol. In the latter cases, the electrons that are produced react rapidly with positive ions e.g.



or



Dorfman<sup>(63)</sup> has observed the solvated electron in both neutral ethanol and methanol and has measured rate constants<sup>(48)</sup> for the reactions of solvated electrons in these solvents with  $\text{H}^+$ ,  $\text{O}_2$ , and  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ .

In a vapor phase study of methanol<sup>(24)</sup>, evidence for an ionic mechanism was obtained from the reasonable agreement of observed yields with those calculated from a mechanism based on mass spectral data for methanol. In the same study, reaction in a xenon-methanol mixture could be quantitatively explained by a charge transfer mechanism. Benzene inhibited hydrogen and formaldehyde formation in the vapor; (formaldehyde was uninhibited in the liquid phase)<sup>(58)</sup>.





d) Deuterated Ethanols.

Burr<sup>(18)(64)</sup> has studied the liquid phase radiolysis of ethanols deuterated in various positions and has found that deuterium substitution in the CH<sub>2</sub> position lowers the total G(hydrogen) to that of CD<sub>3</sub>CD<sub>2</sub>OD. Ethanols with deuterium in the CH<sub>3</sub> and OH positions yield hydrogen in the same quantity as does "light" ethanol. The reactivity of the CH<sub>2</sub> position is strongly indicated by the large yields of 2,3-butanediol, while little or no 1,3- or 1,4-butanediol, ethers, or peroxides have been reported<sup>(17)</sup>. This one site dependence would seem to rule out molecular hydrogen elimination of the type



From the hydrogen isotopic analysis, Burr concludes that hydrogen atoms originate from the CH<sub>2</sub> position. These are said to abstract predominantly (80-90%) from the OH, while 10-20% of the abstraction occurs at the CH<sub>3</sub> site.

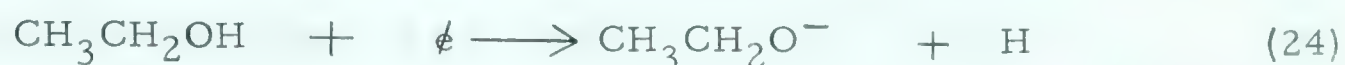
A previous study proved that exchange between the radiolytic hydrogen and that of the substrate molecules was negligible<sup>(65)</sup>.

Comparison of mass spectral data for CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CD<sub>2</sub>OH showed that hydrogen (or deuterium) atoms come mostly from the α-position under mass spectrometer conditions<sup>(64)</sup>.

Lifshitz and Stein<sup>(66)</sup> studied the abstraction of hydrogen atoms from ethanol. Results from isotopic alcohols in aqueous solutions demonstrated that hydrogen atoms attack ethanol in the order α-H > β-H > O-H ≈ O. This order is consistent with the relative bond strengths in the molecule.



A rather large isotope effect was demonstrated in that abstraction of D from  $\text{CH}_3\text{CD}_2\text{OH}$  required 1.7 kcals more than abstraction of H from the  $\text{CH}_2$  position in light ethanol. Stein's results are not in agreement with Burr's postulate that hydrogen atoms originate from the  $\alpha$ -position. They can be explained by



after which the hydrogen atom attacks the alkyl group of a substrate molecule, largely at the  $\alpha$ -position ( $>90\%$ ) to yield a molecule of hydrogen.

Riesz and Burr<sup>(67)</sup> have confirmed negligible abstraction from the OH position by investigating the reactions of D atoms from  $\text{D}_2\text{O}$  containing ethanol.

Dorfman<sup>(47)</sup>, using pulse radiolysis, found that 56% of the hydrogen yield from liquid  $\text{CH}_3\text{CH}_2\text{OD}$  was HD. The HD is said to result from molecular detachment and/or the reverse of Burr's mechanism i.e. primary detachment of the hydroxyl deuterium followed by  $\alpha$ -hydrogen abstraction.

Sullivan and Koski<sup>(68)</sup> conclude from their studies of ESR spectra of photolysed, light and deuterated ethanol and methanol that oxygen containing radicals (i.e.  $\text{CH}_3\text{CHOH}$  and  $\text{CH}_3\text{CH}_2\text{O}$ ) are more stable than alkyl radicals. They also found that the decay of alkyl and  $\alpha$ -alcohol( $\text{RCHOH}$ ) radicals proceeded by hydrogen atom abstraction, which generated alkoxy radicals.

#### e) Deuterated Methanols.

In aqueous solutions of alcohols, the alcohols act as scavengers for the hydrogen atoms and hydroxyl radicals that arise from water decom-

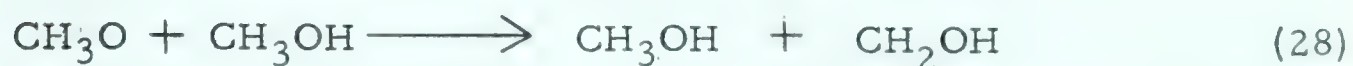
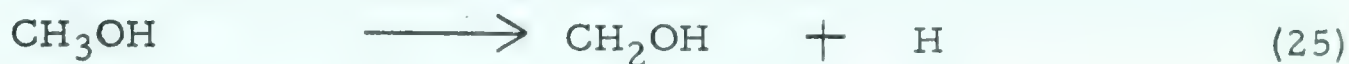




position. A study in the liquid phase has indicated that the attack of such species is largely specific to the hydrogen atoms attached to the carbon of the alcohol.

Nevertheless, in an aqueous radiolytic study of  $\text{CD}_3\text{OH}$ , Riesz and Burr found that hydrogen atoms abstract from both the methyl and the OH positions in methyl alcohol.

Theard and Burton<sup>(59)</sup> found that 78% of the hydrogen from liquid  $\text{CD}_3\text{OH}$  was HD. This was explained by the following processes for light methanol.



Meshitsuka et al<sup>(70)</sup> found 60% HD arising from the radiolysis of  $\text{CH}_3\text{OD}$  while Burr et al<sup>(71)</sup> found 75% HD from the radiolysis of  $\text{CD}_3\text{OH}$ , indicating the importance of both hydrogen atom sites.

#### (F) Photolytic Studies of Alcohols.

Methanol photolysis studies may be considered to be rather far removed from ethanol radiolysis. However, the ethanol and methanol molecules are similar in many respects and although primary photolytic processes need have no connection with primary radiolytic processes, subsequent reactions involving common intermediates may be similar in the two kinds of systems. Therefore, the results obtained from photolysis work



should not be completely ignored when considering radiolytic systems.

In an investigation of the mercury photosensitized reaction of methanol Phibbs and Darwent<sup>(72)</sup> concluded that the primary process was



and stated that

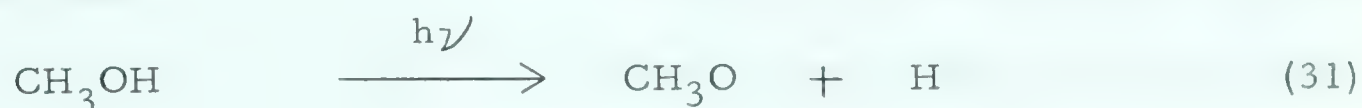


did not occur to any appreciable extent. This hypothesis was partly based on the fact that little HD was produced from the photolysis of  $\text{CH}_3\text{OD}$  and partly upon the observation of ethylene glycol as a major product.

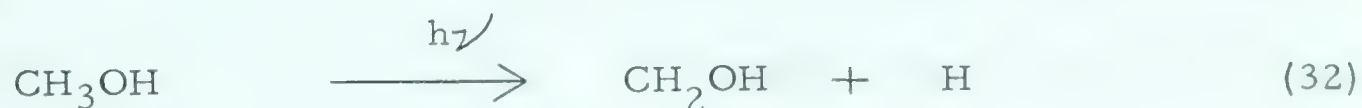
Later photolytic work by Porter and Noyes<sup>(73)</sup> proposed two primary processes one of which was



and the other was



rather than



This difference in the primary step between Phibbs and Darwent's work and the latter study, could be due to the different means employed for decomposition. However, Porter and Noyes' work showed that the primary radicals' identity is not necessarily established through product analysis.

Confirmation of the O-H split in the gaseous Hg photosensitized reaction was obtained from the data of Pottie et. al.<sup>(74)</sup>. They reacted  $\text{CD}_3$  radicals (from photolysis of  $\text{Hg}(\text{CD}_3)_2$ ) with  $\text{CD}_3\text{OH}$ . It was concluded that, at low pressures,  $\text{CH}_3\text{O}$  is the primary radical. The generation of





$\text{CH}_2\text{OH}$  is facilitated by pressure increase through reaction (20).

Shannon and Harrison<sup>(75)</sup> reacted methyl radicals, from the photolysis of acetone, with  $\text{CD}_3\text{OH}$  in the gas phase. At  $182^\circ\text{C}$  the reaction



proceeded four times as fast as



In a liquid phase study, Cher<sup>(76)</sup> reacted  $\text{CD}_3$  radicals with  $\text{CH}_3\text{OH}$  and found that 98% of the abstraction occurred at the methyl group. The switch in the preferred site of attack was attributed to reduction of hydroxyl hydrogen reactivity through hydrogen bonding.

Mercury photosensitized studies have also given evidence that the identity of the primary radicals is not necessarily established by product analysis. Knight and Gunning<sup>(77-79)</sup> found that the products in this type of decomposition are the same as for the radiolysis of methanol and ethanol. As ethylene glycol (from methanol) and 2,3-butanediol (from ethanol) were major products, the presence of appreciable quantities of  $\alpha$ -radicals ( $\text{RCHOH}$ ) was inferred. However, nitric oxide-alcohol mixture data indicated that the primary process was predominantly



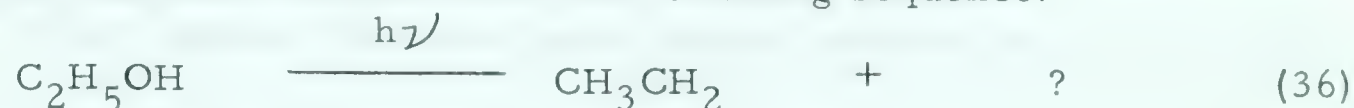
An abstractive process gave rise to  $\alpha$ -radicals.



An investigation of Sullivan and Koski<sup>(68)</sup> has indicated that at low temperatures the reverse of (5) is probable. By means of photolysis, ethanol was decomposed to yield  $\text{C}_2\text{H}_5$ ,  $\text{CH}_3\text{CHOH}$  and other radicals. Decay



of the ethyl and  $\text{CH}_3\text{CHOH}$  radicals was observed and half lives of 2 hours and 1-2 days respectively were measured. Simultaneously, with these decays, there arose an ESR spectrum attributed to the ethoxy radical. The ethoxy radical was said to arise from the following sequence:



The stability of the ethoxy radicals under these conditions is attested to by their half lives of weeks or months at  $77^\circ\text{K}$ .

#### (G) Scope of the Present Work.

The present work deals with various aspects of ethyl alcohol decomposition by gamma rays. Dose dependence and initial yields of products will be reported. The identity and yields of minor products were determined to give a more complete picture of the decomposition. Results from a determination of  $G(\text{water})$ , under conditions where precautions to insure that ethanol's hygroscopic nature would not give misleading high results, will be presented. The effect of two inhibitors on the liquid radiolysis is also to be discussed. Finally, the radiolyses of ethanol and of various deuterated ethanols ("pure" and inhibited) were studied in the vapor and liquid states.





## EXPERIMENTAL

### A) Materials.

#### a) Ethanol

Most commercially available ethanol contains traces of benzene from drying procedures. Benzene has been shown in various cases to affect radiolytic decomposition of organic compounds<sup>(24)(46)(80-82)</sup>. Therefore benzene-free ethanol from Reliance Chemical Co. was used in all experiments involving  $C_2H_5OH$ . The listed specifications were:

Ethanol by volume	not less than	99.90%
Water content	not more than	0.10%
Specific Gravity @ 60 / 60 F	not less than	0.7943
Non-volatile matter (gm/100 ml)	not more than	0.0025
Benzene (gm/100 ml)	not more than	0.0007

Gas chromatographic analysis of the alcohol on Carbowax 1500 on Fluoropak, Ucon on Celite, and n-didecyl phthalate on Fluoropak columns on a Burrell model K-2 chromatographic unit (to be described later) showed no detectable impurities except water (0.1%). Polarographic analysis on a Leeds Northup Speedomax G model polarograph usually confirmed the absence of acetaldehyde as an impurity. However, occasional samples showed approximately 0.01 mole% acetaldehyde.

For the first set of irradiations a quantity of the material was distilled into the vacuum system (described below), degassed thoroughly, and used without further purification. The second set of samples and all



samples thereafter were carried out with ethanol that had been treated to remove as much water as possible, using ordinary chemical means.

Initial attempts at removing the water involved the use of various drying agents such as Drierite and  $\text{CaH}_2$ ; however, analysis on a Carbowax 1500 on Fluoropak column proved these to be largely ineffective. The procedure selected for the removal of the water was as follows<sup>(83)</sup>. Approximately 800 ml. of the 99.9% ethanol was placed in a vessel connected to a reflux condenser. Six gms. of freshly cut sodium metal and 26 gms. of diethyl phthalate (purified grade) were added and the mixture was refluxed for two hours. Immediately after refluxing, the ethanol was distilled slowly. The first 50 ml. of the distillate were discarded. The next 50-100 ml. were collected and immediately distilled into the vacuum system. Vigorous bumping prevented more of the alcohol from being recovered. During refluxing and distillation, either hydrogen or purified nitrogen passed through charcoal and silica gel traps maintained at  $-196^\circ\text{C}$  and through the remainder of the distillation apparatus, including the collecting vessel. In the refluxing and distillation apparatus proper, all connections consisted of ungreased ground glass joints.

After degassing at  $-112^\circ\text{C}$  (ethanol "slush" temperature) a sample of the ethanol was removed from the vacuum system and tested for water content on a Carbowax 1500 column. If analysis showed more than  $0.01 \pm 0.002\%$  water the ethanol was discarded; if the water content was less than  $0.01\%$  (usually less than  $0.005\%$ ) the ethanol was used in radiolysis experi-





ments. The limit of detectable water was 0.002%.

A different purification technique was used for the ethanol radiolized to "small conversions". Before purification the alcohol contained 0.009% acetaldehyde. As acetaldehyde is a product of the radiolysis of ethanol and it has been shown<sup>(30)</sup> to decrease the yield of hydrogen, special precautions to insure its absence at the beginning of irradiation were taken. (A dose of  $\approx 0.15 \times 10^{20}$  e.v./ml. would generate 0.009% acetaldehyde). A modification of the procedure outlined by Wild<sup>(84)</sup> for the preparation of 2,4-dinitrophenylhydrazones was employed to remove any aldehyde present. Two gms. of 2,4-dinitrophenylhydrazine were dissolved in 20 ml. of concentrated sulphuric acid and added to 2000 ml. of 99.9% ethanol; this solution was refluxed for three and a half hours. Then it was distilled (leaving behind the high boiling sulphuric acid and hydrazone) to a second vessel from which it was distilled from diethyl phthalate and sodium, in the usual manner, after the customary one and a half hours refluxing. This ethanol was immediately transferred to the vacuum system where it was degassed and stored in a Pyrex glass reservoir, from which samples for water and acetaldehyde analysis were taken. The water content was less than 0.005%. Polarography showed no detectable acetaldehyde (limit of detection  $\approx 0.004$  mole %).

The 2,4-dinitrophenylhydrazine procedure was only carried out for this series of "very low dose runs", since for higher doses, product acetaldehyde would have been inevitably present in detectable amounts after the initiation of the  $\gamma$ -ray bombardment.



Experiments involving deuterated alcohols were performed with substrates obtained commercially from Merck, Sharp and Dohme Ltd., Montreal. Losses due to purification techniques, the probability of introducing sizable quantities of water (because of the extremely hygroscopic nature of ethanol), and hydrogen-deuterium exchange in the OD position, precluded attempts at purification. For these reasons and the high cost of the samples, they were used as they were received from the supplier. However, aliquots of each alcohol were removed and analysed for water, acetaldehyde and other impurities by gas chromatography. Another portion was taken for isotopic purity analysis by nuclear magnetic resonance (NMR) on a Varian Associates Model A-60 Analytical NMR Spectrophotometer. Results of these various analyses are presented in Table II, page 32.

The deuterated alcohols were synthesized by Merck, Sharp, & Dohme as follows<sup>(85)</sup>:

- (1)  $\text{CH}_3\text{CH}_2\text{OD}$ : prepared by the hydrolysis of diethyloxalate with deuterium oxide followed by repeated equilibration with  $\text{D}_2\text{O}$  and fractional distillation.
- (2)  $\text{CD}_3\text{CD}_2\text{OD}$ : prepared by the exchange of  $\text{CD}_3\text{CD}_2\text{OH}$  prepared as described in (3) followed by careful distillation.
- (3)  $\text{CD}_3\text{CD}_2\text{OH}$ : prepared by reacting ethyl- $\text{d}_5$  bromide with silver acetate to form ethyl- $\text{d}_5$  acetate followed by hydrolysis with  $\text{NaOH}$  and fractional distillation.
- (4)  $\text{CD}_3\text{CH}_2\text{OH}$ : prepared by the reduction of acetyl- $\text{d}_3$  chloride with lithium aluminum hydride in ether followed by fractional distillation.
- (5)  $\text{CH}_3\text{CD}_2\text{OH}$ : prepared by the reduction of acetyl chloride with lithium





TABLE II - 1  
ANALYSIS OF DEUTERATED ALCOHOLS.

Alcohol	Mole % Isotopic Purity	%H <sub>2</sub> O	Other Impurities <sup>4</sup>
C <sub>2</sub> H <sub>5</sub> OD	>99 % for OD	0.09	3 impurities totaling 0.2%, one of which is acetal $\approx$ 0.15%, the other 2 not identified.
C <sub>2</sub> D <sub>5</sub> OD	99.5% for OD 99.6% for CD <sub>2</sub> 99.6% for CD <sub>3</sub>	0.08	2 impurities totaling 0.15%, one of which is acetal $\approx$ 0.1%, the other not identified.
C <sub>2</sub> D <sub>5</sub> OH <sup>1</sup>	99.2% for CD <sub>2</sub> 99.4% for CD <sub>3</sub>	0.10	0.5% ether, 0.1% acetal, and 0.1% unidentified impurity.
C <sub>2</sub> D <sub>5</sub> OH <sup>2</sup>	98.7% for CD <sub>2</sub> 99.4% for CD <sub>3</sub>	— <sup>3</sup>	$\approx$ 1% acetal and $\approx$ 10% unknown impurity.
CH <sub>3</sub> CD <sub>2</sub> OH	96.3% for CD <sub>2</sub>	0.5	0.1% acetal and $\approx$ 0.1% unknown impurity.
CD <sub>3</sub> CH <sub>2</sub> OH	99.9 % for CD <sub>3</sub>	0.1	0.15% acetal and $\approx$ 0.15% unknown impurity.

## Notes:

- 1 and 2 Two different samples of C<sub>2</sub>D<sub>5</sub>OH from Merck, Sharp and Dohme were used.
- 3 No water analysis due to interference from large ( $\approx$  10%) unknown impurity.
- 4 "Other impurity" results in the last column were obtained by G C using Carbowax 1500 on Fluoropak and n-didecyl phthalate on Fluoropak columns.
- 5 The unidentified impurity in the first quantity of C<sub>2</sub>D<sub>5</sub>OH and that in the CH<sub>3</sub>CD<sub>2</sub>OH and CD<sub>3</sub>CH<sub>2</sub>OH appear to be the same compound.



aluminum deuteride in ether followed by careful fractionation through an efficient column.

All alcohols were carefully dried with freshly ignited calcium oxide.

b) Benzene.

The benzene used was Phillips Research Grade. Silica gel and Carbowax 1500 columns showed approximately 0.3% hydrocarbon impurities and 0.4% water. The benzene was distilled in a conventional distillation apparatus (ungreased ground glass joint connections, the middle third being retained and distilled into a reservoir in the vacuum system where it was degassed thoroughly). A sample taken from the reservoir showed no detectable hydrocarbon impurities and less than 0.004% water.

c) 1,3-Pentadiene.

The 1,3-pentadiene was from Columbia Organic Chemicals Co. Inc. A portion was distilled into the vacuum system leaving behind  $\approx 30\%$  which became deeply colored. The pentadiene in the reservoir was colorless. A silica gel chromatogram showed the pentadiene was  $> 95\%$  pure.

d) Gases for Calibration and Identification.

The gases used were from various suppliers and needed no purification for purposes of identification and calibration. All were greater than 95% pure. For calibration of the gas chromatographs an impurity correction was applied when necessary.

The gases and their suppliers are listed in a table of materials given below.





e) Liquids for Calibration and Identification.

These are listed in the materials table as well. For identification purposes they were used as they came from the manufacturer.

For calibration purposes, the chemicals were analyzed by gas chromatography or other means, and if found to be of 90% purity or better they were used without purification (impurity corrections being applied to the calibrations). If the chemical was less than 90% pure or analysis was uncertain, the chemical was purified by appropriate means until sufficient and quantitative purity was obtained.

TABLE II-2

MATERIALS USED

1	Acetal	May and Baker Ltd.	
1a	Acetal	Eastman Kodak (Yellow Label)	
2	Acetaldehyde	Eastman Kodak (White Label)	
3	Acetylene	Matheson of Canada Ltd.	
4	Apiezon N, L & T	Metropolitan-Vickers Electrical Co. Ltd.	
5	Benzene	Phillips Petroleum Co. (Research Grade)	(1)
6	n-Butane	Phillips Petroleum Co. (Research Grade)	
7	1,3-Butanediol	Eastman Kodak (White Label)	
8	1,4-Butanediol	Eastman Kodak (Yellow Label)	
9	2,3-Butanediol	Anachemia Chemicals Ltd.	
10	d,l-2,3-Butanediol	Sample compliments of Prof. Anet of the University of Ottawa	



TABLE II-2 - Continued

11	Carbon Monoxide	Matheson of Canada Ltd.	
12	Carbowax 20M	F & M Scientific Corporation	
13	Carbowax 1500	Carbide & Carbon Chemicals Co. Ltd.	
14	Carbowax 1540	Carbide & Carbon Chemicals Co. Ltd.	
15	Carbowax 4000	Carbide & Carbon Chemicals Co. Ltd.	
16	Carbowax 4000 Stearate	F & M Scientific Corporation	
17	Carbowax 6000	Carbide & Carbon Chemical Co. Ltd.	
18	Celite (Kromat CE)	Burrell Corporation	
19	Charcoal	Burrell Corporation (high activity)	
20	Chromotropic Acid	K & K Laboratories Inc.	
21	Deuterium	Matheson of Canada Ltd.	
22	Deuterium Oxide	Bio-Rad Laboratories	
23	Dimedone	Eastman Kodak (White Label)	
24	2,4-Dinitrophenyl hydrazine	Eastman Kodak (White Label)	
25	Ethane	Phillips Petroleum Co. (Research Grade)	
26	Ethanol	Reliance Chemical Co.	(2)
27	Deuterated Ethanol		(3)
a	$\text{CH}_3\text{CH}_2\text{OD}$	Merck, Sharp & Dohme Ltd.	
b	$\text{CD}_3\text{CD}_2\text{OD}$	Merck, Sharp & Dohme Ltd.	
c	$\text{CD}_3\text{CD}_2\text{OH}$	Merck, Sharp & Dohme Ltd.	
d	$\text{CH}_3\text{CD}_2\text{OH}$	Merck, Sharp & Dohme Ltd.	
e	$\text{CD}_3\text{CH}_2\text{OH}$	Merck, Sharp & Dohme Ltd.	





TABLE II-2 - Continued

28	Ethylene	Phillips Petroleum Co. (Research Grade)	
29	Ethylene-d <sub>4</sub>	Merck, Sharp & Dohme Ltd.	
30	Ethylene glycol	Eastman Kodak (White Label)	
31	Ethyl phthalate	Fischer Scientific Co.	
32	Ferrous Ammonium Sulphate	Allied Chemical Corp.	
33	Fluoropak 80	The Fluorocarbon Co.	
34	Formaldehyde Solution	Fischer Scientific Co.	
35	Haloport F	F & M Scientific Co.	
36	Helium	Matheson of Canada	
36a	Helium	Air Reduction Canada Ltd.	
37	Hexadeutero Ethane	Merck, Sharp & Dohme Ltd.	
38	Lithium Chloride	Fischer Scientific Co.	
39	Lithium Hydroxide	Fischer Scientific Co.	
40	Mannitol	Eastman Kodak (White Label)	
41	Methane	Phillips Petroleum Co. (Research Grade)	
42	Octadeutero Propane	Merck, Sharp & Dohme Ltd.	
43	Octoil - S	Sample compliments of C.I.L. (Edmonton)	
44	1,3-Pentadiene	Columbia Organic Chemicals Co. Inc.	(4)
45	Propane	Phillips Petroleum Co. (Research Grade)	
46	1,2-Propanediol	Eastman Kodak (White Label)	
47	1,3-Propanediol	Eastman Kodak (White Label)	
48	Pluronic P84	Wyandotte Chemicals Corp.	



TABLE II-2 - Continued

49	sec.-Butyl alcohol	Eastman Kodak (White Label)	
50	Silica Gel	Burrell Corp. (Medium Activity)	
51	Silicone Grease	Dow Corning Corp.	
52	Silicone Oil 710	Dow Corning Corp.	
53	Sodium Metal	British Drug House	
54	Sorbitol-Silicone Oil	F & M Scientific Corp.	
55	Teflon T-6	Analytical Engineering Laboratories Inc.	
56	THEED	F & M Scientific Corp.	
57	Tri-O-tolyl phosphate	Eastman Kodak (Yellow Label)	
58	Ucon LB-1800	Carbide & Carbon Chemicals Co.	
59	Water		(5)

(1) See p. 33 for purification and analysis.

(2) See p. 28 for purification and analysis.

(3) See p. 32 for purification and analysis.

(4) See p. 33 for purification and analysis.

(5) Doubly distilled. First distillation from potassium permanganate.

## B) APPARATUS

### a) High Vacuum System.

The high vacuum apparatus used during the course of the experiments was constructed of Pyrex glass securely clamped to a metal frame





consisting of "Dexion" angle iron and "Flexiframe" rods. This frame in turn was affixed to a wooden table.

All glass used in the manufacture of the vacuum system was washed with soap and water (more rigorous cleaning procedures were used for reservoirs, sample cells, etc.).

In the section to follow, an attempt will be made to depict and explain the vacuum system. However, as might be expected, such a treatment will deal only with the more permanent and basic aspects of the system, as it was continually being modified for various purposes during the period of investigations.

i) Main Manifold.

The main manifold served essentially as a principal artery to which various other manifolds were joined. A schematic diagram of the main manifold is given in Figure II-1, page 39.

Evacuation of the system was effected by a two stage mercury diffusion pump in conjunction with a Welch Duo Seal, two stage high vacuum pump. Trap  $T_1$  in Figure II-1 was always immersed in liquid nitrogen while the mechanical pump was running, to trap out materials that could interfere with its efficient operation.


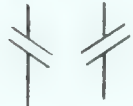
Dow Corning High Vacuum silicone grease was used for all stop-cocks and ground glass joints. Loc-Lube Grease #2 from Burrell Corp. was found to be more satisfactory for ball and socket joints.

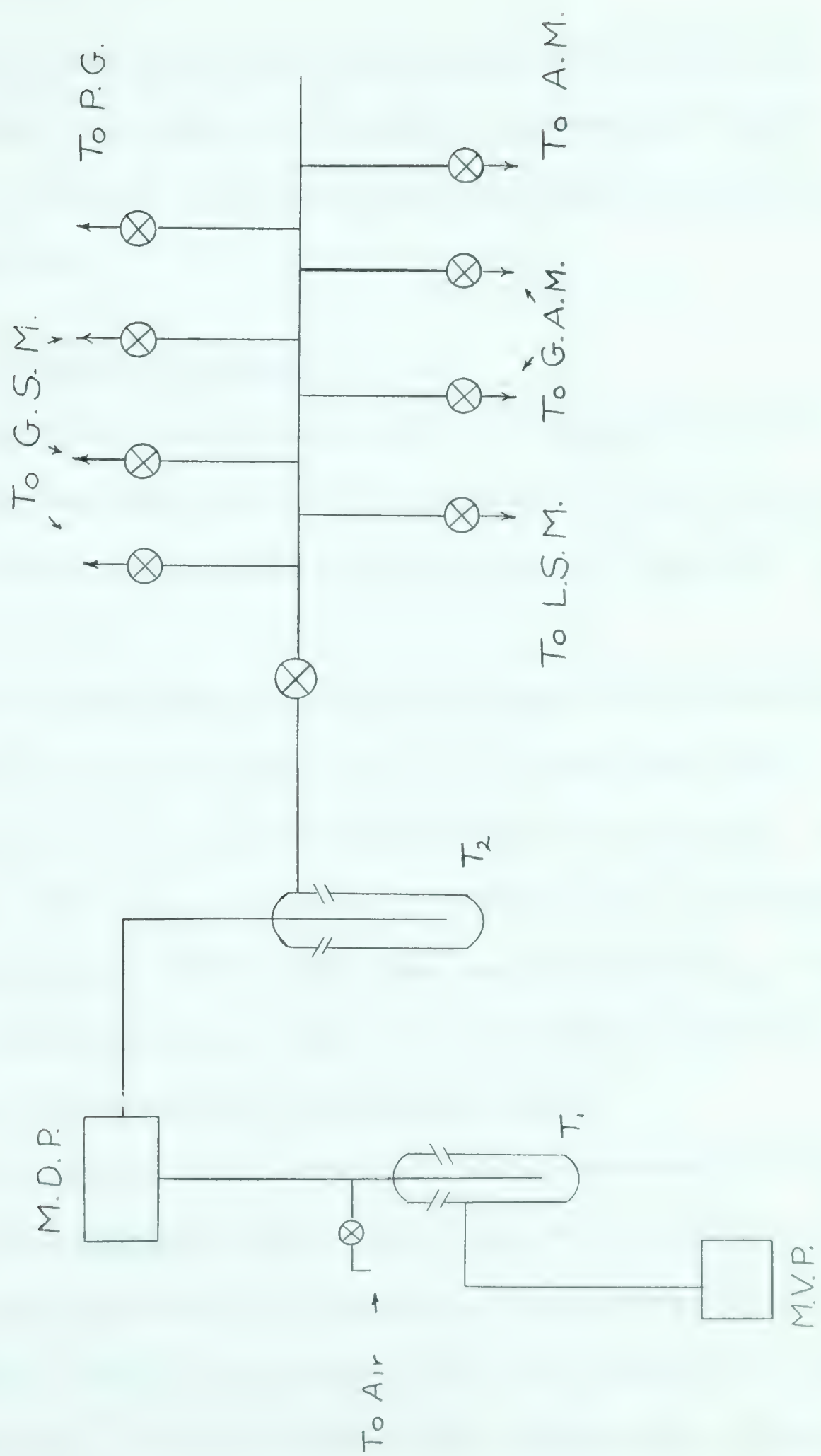
The mercury in the diffusion pump was triply distilled from

Figure II-1

MAIN MANIFOLD

(Not to Scale)

A.M..	:	Auxiliary Manifold
G.A.M.	:	Gas Analysis Manifold
G.S.M.	:	Gas Storage Manifold
L.S.M.	:	Liquid Sampling Manifold
M.D.P.	:	Mercury Diffusion Pump
M.V.P.	:	Mechanical Vacuum Pump
P.G.	:	Pirani Gauge
T	:	Trap
	:	Vacuum Stop-cock
	:	Ground Glass Joint







Engelhard Industries.

The Pirani Gauge was from Consolidated Electrodynamics (Type GP-110) and was capable of measuring pressures down to about 0.5 microns. The probe of the gauge was sealed to the Pyrex system by Edwards Picien Wax.

ii) Liquid Sampling Manifold.

This system was initially used for the preparation of liquid samples only but was later adapted for the preparation of gas samples as well. The ordinary liquid sampling system is shown in Figure II-2, page 41.



Immediately after purification the ethanol was introduced into the reservoir  $R_1$  through the connection G.G.J1 (ground glass joint). Before being joined to the vacuum system the Pyrex reservoir " $R_1$ " had previously been cleaned by a 5:2 mixture of sulphuric:nitric acid mixture that had been heated to  $100^{\circ}\text{C}$ . This treatment was followed by at least 12 washings with distilled water followed by four washings with doubly distilled water (first distillation from permanganate).

The ordinary liquid sample cells were constructed of Pyrex glass tubing of the appropriate size to give a tight fit in the various irradiation blocks used (see section on Irradiation). The bottoms of these cells were deliberately blown with thin glass walls in accordance with the sample analysis procedure. Details of these sample cells are given in Figure II-3A. The cleaning procedure and the possible consequences of improper cleaning

FIGURE II-2

LIQUID SAMPLING MANIFOLD

(Not to Scale)

C.T. 1,2	:	Calibrated Tubes
F.V. 1,2	:	Mercury Float Valves
M.M.	:	Main Manifold
R <sub>1,2</sub>	:	Reservoirs
S.C.	:	Sample Cells
Vac.	:	Vacuum
	:	Stopcock
	:	Ground Glass Joint

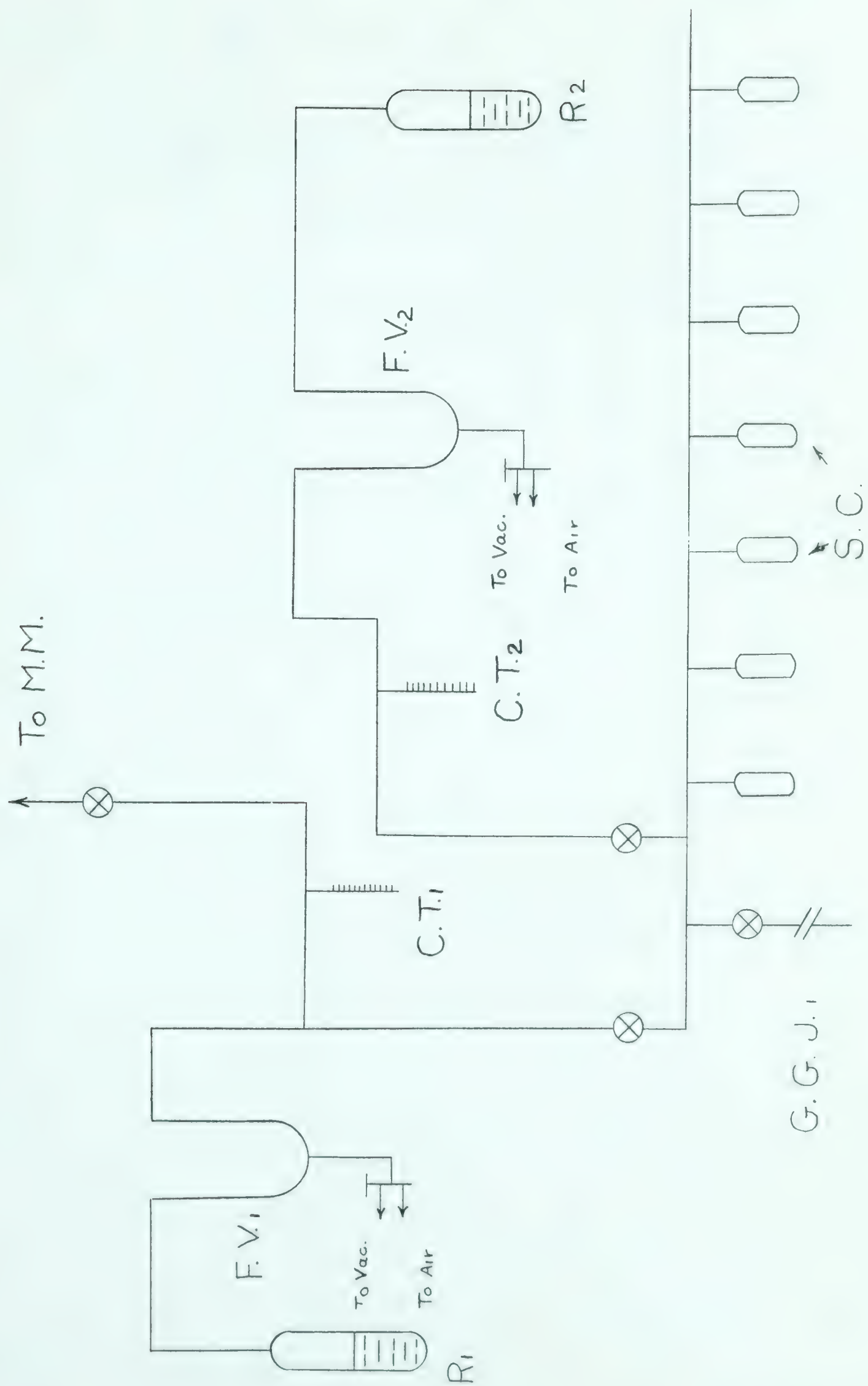


FIGURE II-3

VARIOUS CELLS FOR SAMPLE PREPARATION.

(Not to Scale)

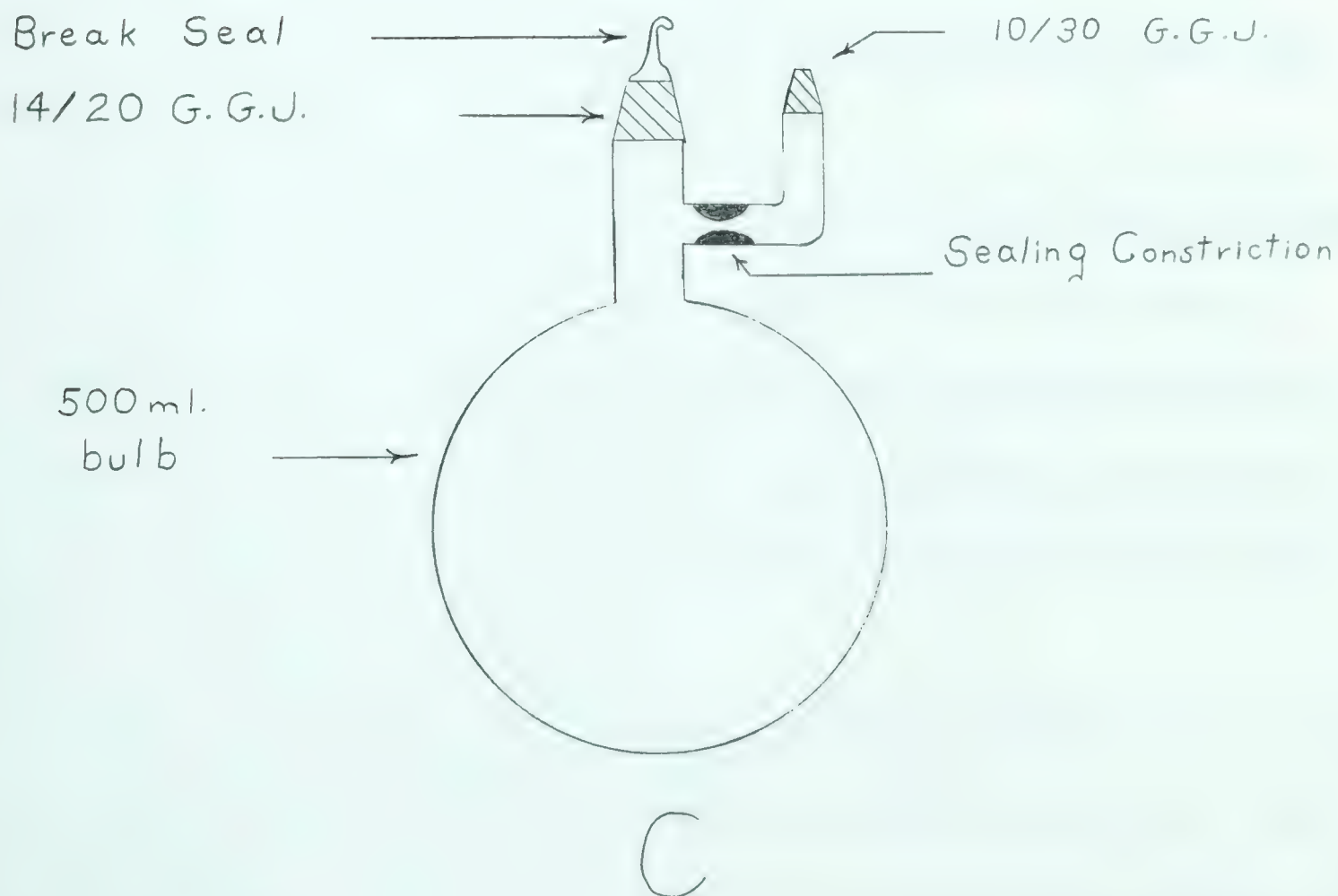
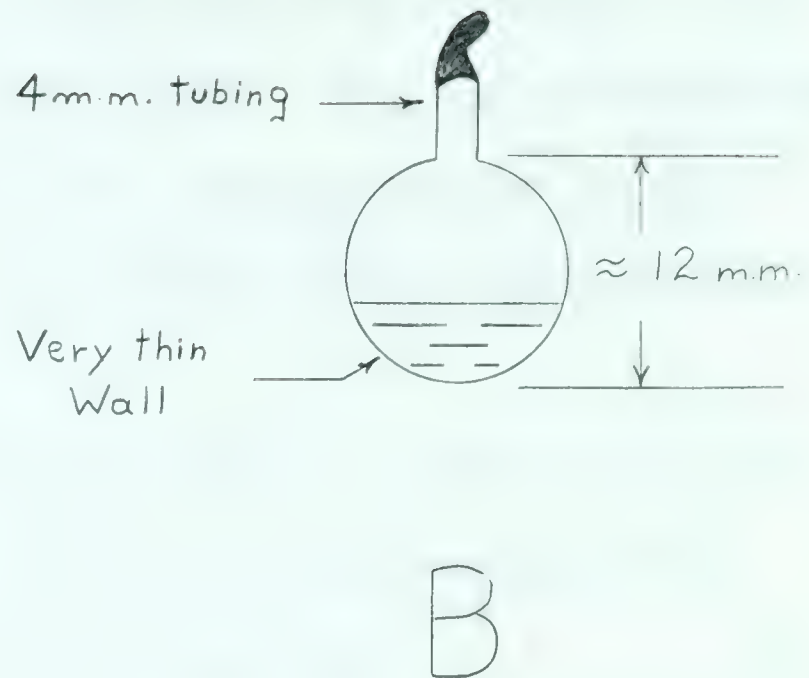
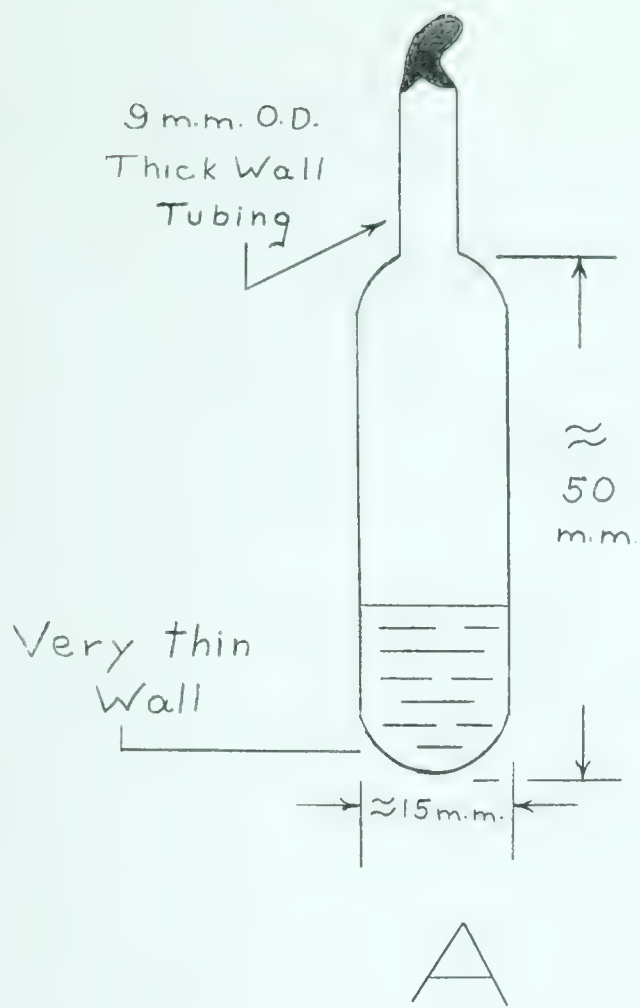
A. Usual Liquid Sample Cell

B.. Water Analysis Cell

C. Gas Phase Sample Cell

G.G.J. : Ground Glass Joint







will be discussed later.

For samples to be used to determine  $G(H_2O)$  a special type of cell was made which is shown in Figure II-3(B). Very thin walled spherical bulbs were blown at the end of 4 mm.O.D. tubing and fused to the liquid sampling manifold. These samples were filled to  $\approx 1/5$  of their volume capacity.

The preparation of gas phase samples involved a vessel of the type depicted in Figure II-3(C). A rigorous cleaning procedure (to be described later) was employed for all gas sample cells.

The system outlined in Figure II-2 was utilized for ethanol-benzene samples in the range from 5-100% benzene. For samples utilizing less than 5% benzene, the benzene was measured in a microliter syringe and transferred into a vessel of the type shown in Figure II-4(A). This vessel was immediately affixed to the sampling system via the ground glass joint G.G.J.1 of Figure II-2.

$C.T_1$  and  $C.T_2$  of Figure II-2 were Pyrex tubes with graduations that were calibrated by means of a micro pipette. These were used to measure the volume of the sample being prepared at a known temperature. At the volume of the samples prepared, the volume calibration was accurate to  $\pm 1\%$ . The volume of ethanol or inhibitor was measured while the liquid was immersed in an ice-bath ( $0^\circ C$ ).

For benzene inhibition runs reservoir  $R_2$  of Figure II-2 contained Phillips Research Grade benzene purified as described on page 33. Later the benzene was replaced by 1,3-pentadiene, whose purification and analysis





are outlined on page 33.

The mercury float valves governing the flow of ethanol and benzene were operated by three way stop-cocks, two of whose paths led to air and the auxiliary vacuum system and the third to the float valve.

The volumes of the systems in which the ethanol and benzene were measured were small enough so that the amount of substance in the vapor phase was negligible compared to that measured in the liquid state.

Two different systems were used to prepare samples for water analysis. The first type of operation and measurement involved the use of the apparatus shown in Figure II-2 where the amount of sample was measured in the graduated  $C.T_1$ . The cells used were of the type shown in Figure II-3(B).

In the second and more accurate procedure the quantity of ethanol was determined by pressure-volume measurements in a system involving a 2 liter bulb connected to a manometer. This apparatus is shown in Figure II-4(B).

Because of the high vapor pressure of 1,3-pentadiene at room temperature, the pressure-volume type of measurement could be used for samples containing  $< 20\%$  1,3-pentadiene in a 2 ml. sample. For 1,3-pentadiene concentrations  $> 20\%$ , liquid-volume measurements at a known temperature were carried out in a system analagous to that of Figure II-2.

## FIGURE II-4

## A. BENZENE SAMPLING CELL

G.G.J. : Ground Glass Joint

B. SYSTEM FOR MEASURING SUBSTANCES BY THE PVT  
METHOD.

(Not to Scale)

F.V.1,2 : Mercury Float Valves


G.G.J. : Ground Glass Joint

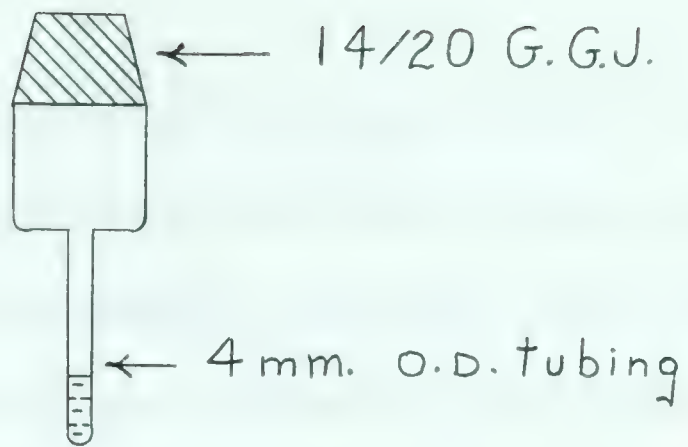
M.M. : Main Manifold

M.R. : Mercury Reservoir

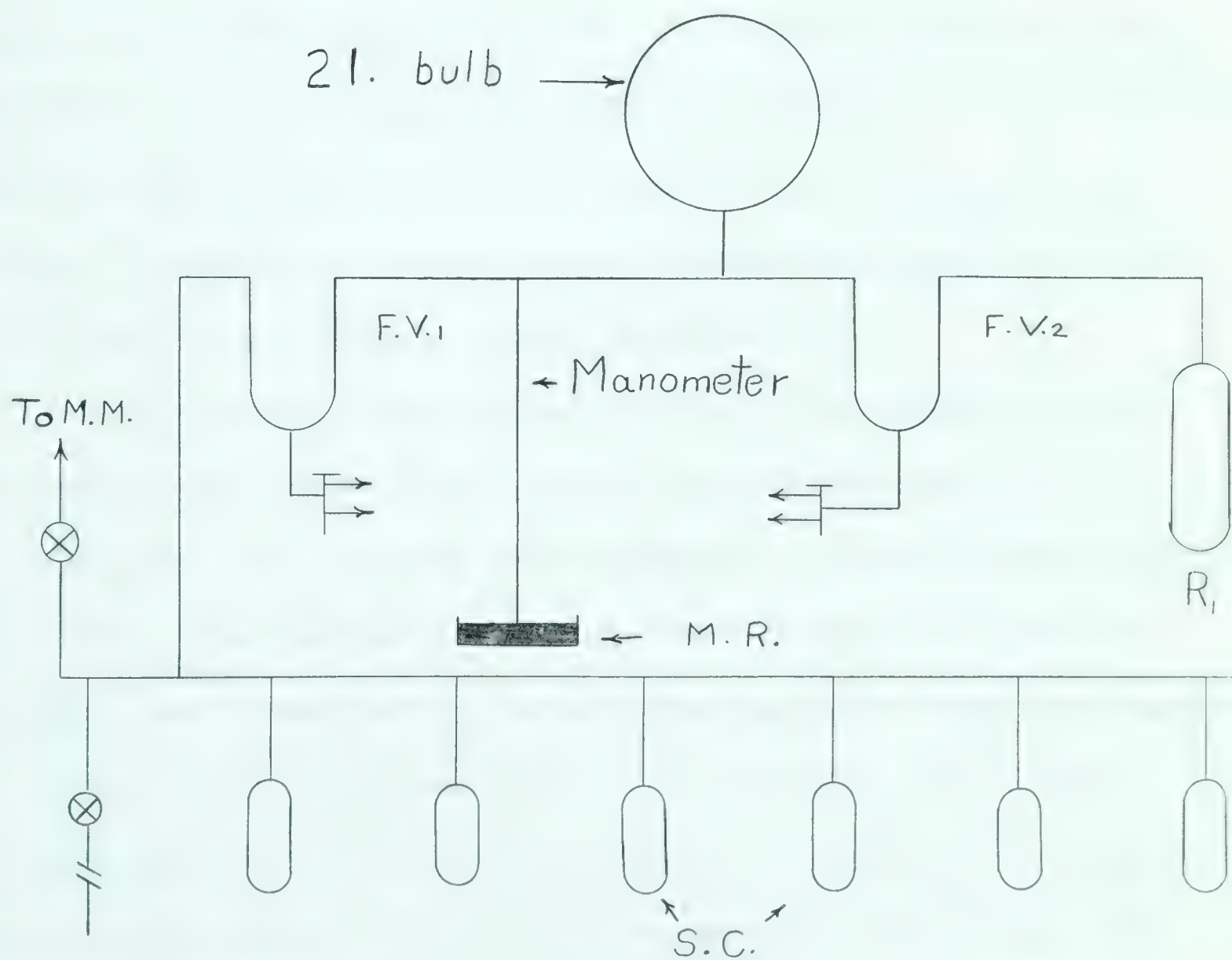
S.C. : Sample Cells

 : Stopcock

 : Ground Glass Joint



A



B





### iii Gas Sampling Manifold.

This manifold (shown schematically in Figure II-5) served a dual purpose. First, it was the means by which samples of gases were measured to calibrate the gas chromatographs. Secondly, it was used to prepare samples of ethylene for vapor phase dosimetry (See Dosimetry section below).

Introduction of the gases into their individual reservoirs (1 liter Pyrex bulbs) was through G.G.J.1 of Figure II-5, which for this purpose was actually a 12/2 socket joint. To exclude air from the system the cylinder containing the gas in question was connected to a "mercury bubbler" (Figure II-6(A)), which in turn was fitted to G.G.J.1. After preliminary flushing, by-passing the sampling manifold through the main manifold, one of the reservoirs was filled to an appropriate pressure.

To obtain a sample for calibration, the same gas trap as was used to obtain gas aliquots from irradiated samples was connected to G.G.J.1. (The two types of gas traps that were employed are shown in Figures II-6(B) and II-6(C)). The sampler was evacuated through the main manifold and then was opened to the manifold containing the gas and an aliquot was trapped off. The pressure trapped was read off the manometer. The sampler was then connected to the gas chromatographic system and a chromatograph was run under conditions identical to those used for a portion of gas taken from an irradiated sample.

For gas phase dosimetry the volume of the reservoirs was accurately measured. Phillips Research Grade ethylene was put in the



reservoirs and manifold to a pressure of approximately 380 mm. (again using the "mercury bubbler"). Then it was degassed using the traps,  $T_1$  and  $T_2$ , for trap to trap distillation while the ethylene was being pumped on through the main manifold. When thoroughly degassed, it was stored in the reservoirs. Pressure, volume and temperature measurements gave the amount of ethylene in each bulb. For dosimetry the ethylene in a reservoir was completely transferred to a vessel of the type shown in Figure II-3(C).

#### iv) Gas Analysis Manifold.

This manifold was modified, depending on whether a liquid phase or a gas phase sample was to be analyzed.

The arrangement for liquid samples is shown in Figure II-7. "A" is a trap through which Purified Grade nitrogen could be introduced over the sample after gas analysis, to prevent the possible oxidation of any products during liquid product analysis. The sample to be analyzed was placed, thin bottom up and with a magnetic breaker placed on top of it, in the trap "B". This trap had a side arm and ampoule attached to it, into which the degassed sample was distilled after gas analysis.  $T_1$  and  $T_2$  were conventional cold traps into which the sample was distilled while the gases were being Toeplered. "C" was a cold finger which was needed to help accomodate large volume (10 ml.) liquid samples used for short exposure runs. A combination Toepler pump-McLeod Gauge was used to collect and measure the product gases. This gauge was capable of measuring pressures down to 0.1 microns. An aliquot of gases or the total gas fraction

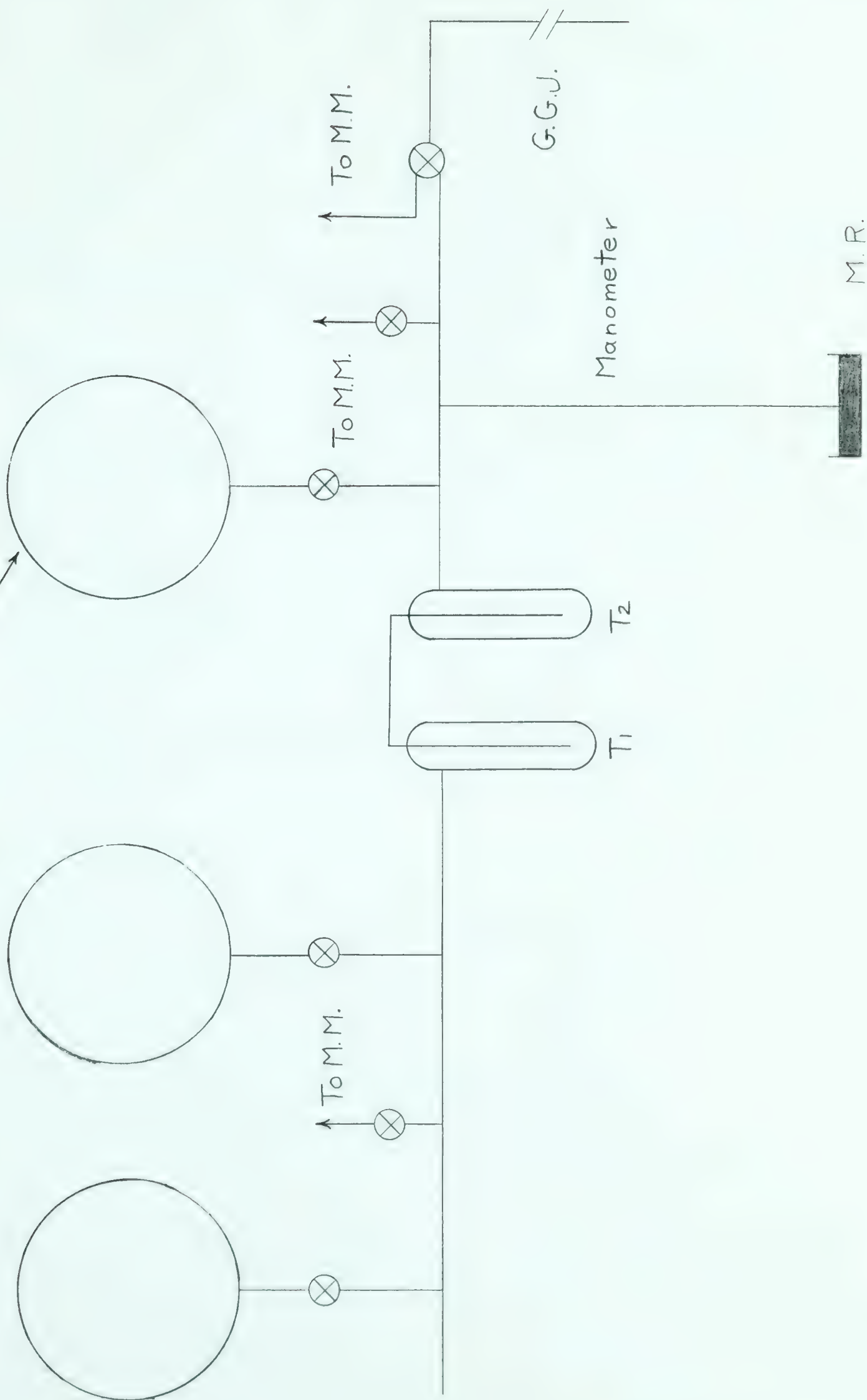
## FIGURE II-5

## GAS SAMPLING MANIFOLD

(Not to Scale)

M.M.	:	Main Manifold
M.R.	:	Mercury Reservoir
T <sub>1,2</sub>	:	Traps
G.G.J.	:	Ground Glass Joint

1 liter bulb





## FIGURE II-6

## A. MERCURY "BUBBLER"



:

Vacuum Stopcock

## B. GAS SAMPLER FOR GAS CHROMATOGRAPHIC ANALYSIS (I).

S.S.

:

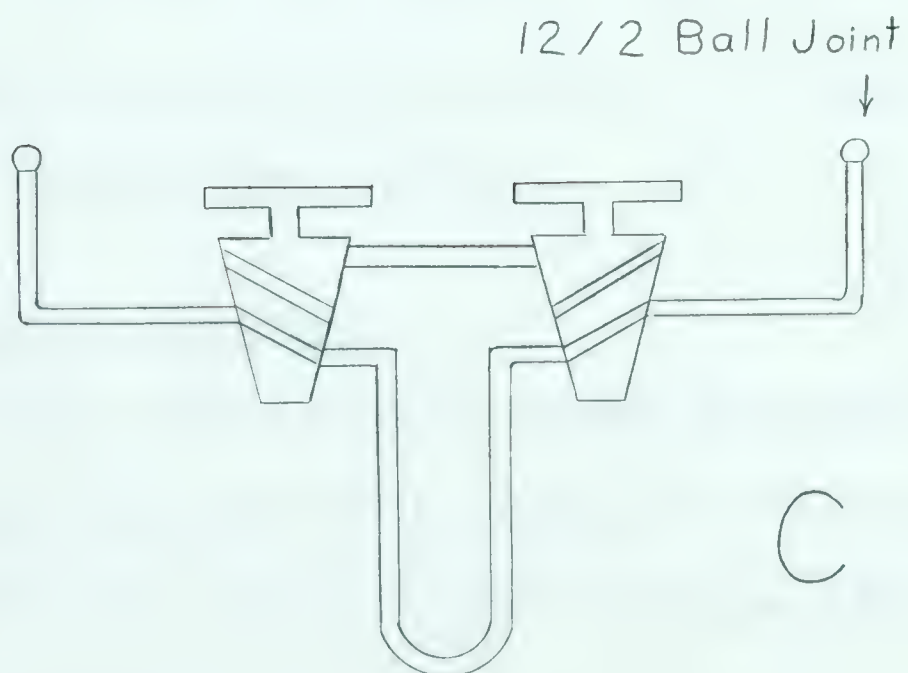
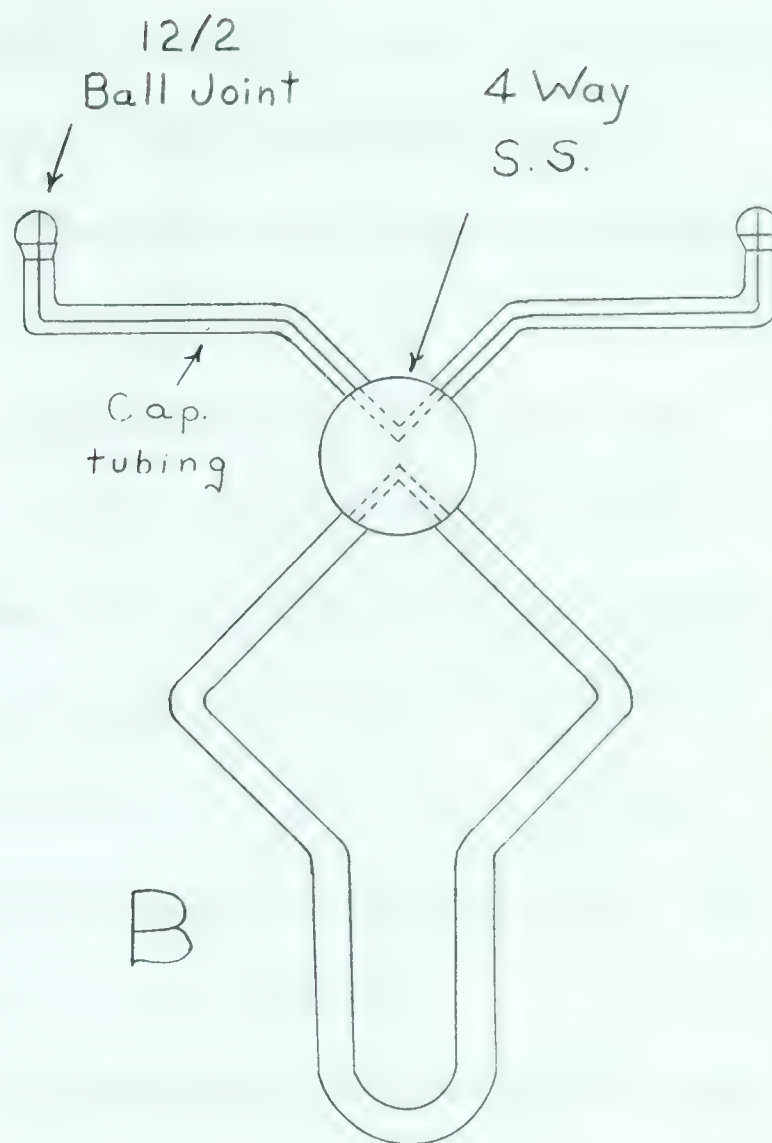
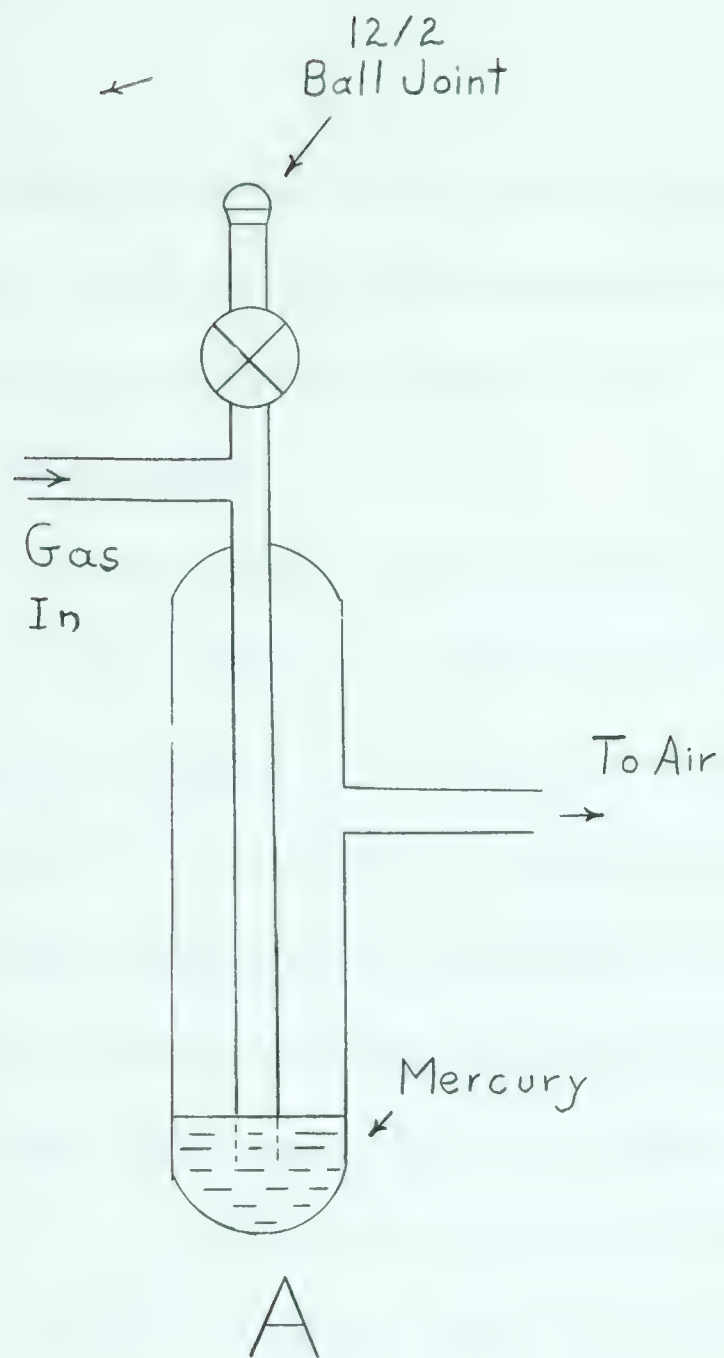
Stopcock

Cap. Tubing

:

Capillary Tubing

## C. GAS SAMPLER FOR GAS CHROMATOGRAPHIC ANALYSIS (II).





(depending upon the vapor pressures and amounts of the gases) was collected in the trap at the top of the McLeod Gauge. This trap was of the type shown in either Figure II-6(B) or (C). The gas mixture was immediately chromatographed.

For vapor phase samples, some changes in the system were necessary. These are shown in Figure II-8. The bulb containing the radiolized sample ("B" in the figure) was of the type shown in Figure II-3(C). Ampoule "A" contained the sample after the gases had been removed and this was sealed off for liquid product analysis at a later time. "C" was a "U" trap that contained Molecular Sieves during ethylene dosimetry runs but which was empty during an irradiated alcohol analysis.

As the gas mixtures from the deuterated alcohols required mass spectrometric analysis, another type of gas trap was necessary. Figure II-9 shows one type used. Another kind, in which the 100 ml. bulb was replaced by a tube, was also employed. When this type of trap was used, it was evacuated through the main manifold rather than the auxiliary used for the gas traps described previously.




#### v) Auxiliary Manifold.

This manifold served to operate the various mercury float valves and to evacuate the Toepler-McLeod gauge and the gas samplers. Sufficiently good vacuum for this system was obtained using a Welch Duo Seal, single stage Vacuum Pump.

FIGURE II-7

## GAS ANALYSIS MANIFOLD FOR LIQUID PHASE SAMPLES.

(Not to Scale)

A	:	Trap for introducing nitrogen above samples that were analyzed for gases.
B	:	Trap with ground glass joint containing sample to be analyzed for gases.
C	:	Finger used for large volume samples.
D	:	Gas trap of the type shown in Figure II-6(B).
E	:	Combined Toepler Pump-McLeod Gauge.
A.M.	:	Auxiliary Manifold
M.M.	:	Main Manifold
$T_{1,2}$	:	Cold Traps.
	:	Ground Glass Joint (24/40)
	:	Two Way Stopcock
	:	Three Way Stopcock



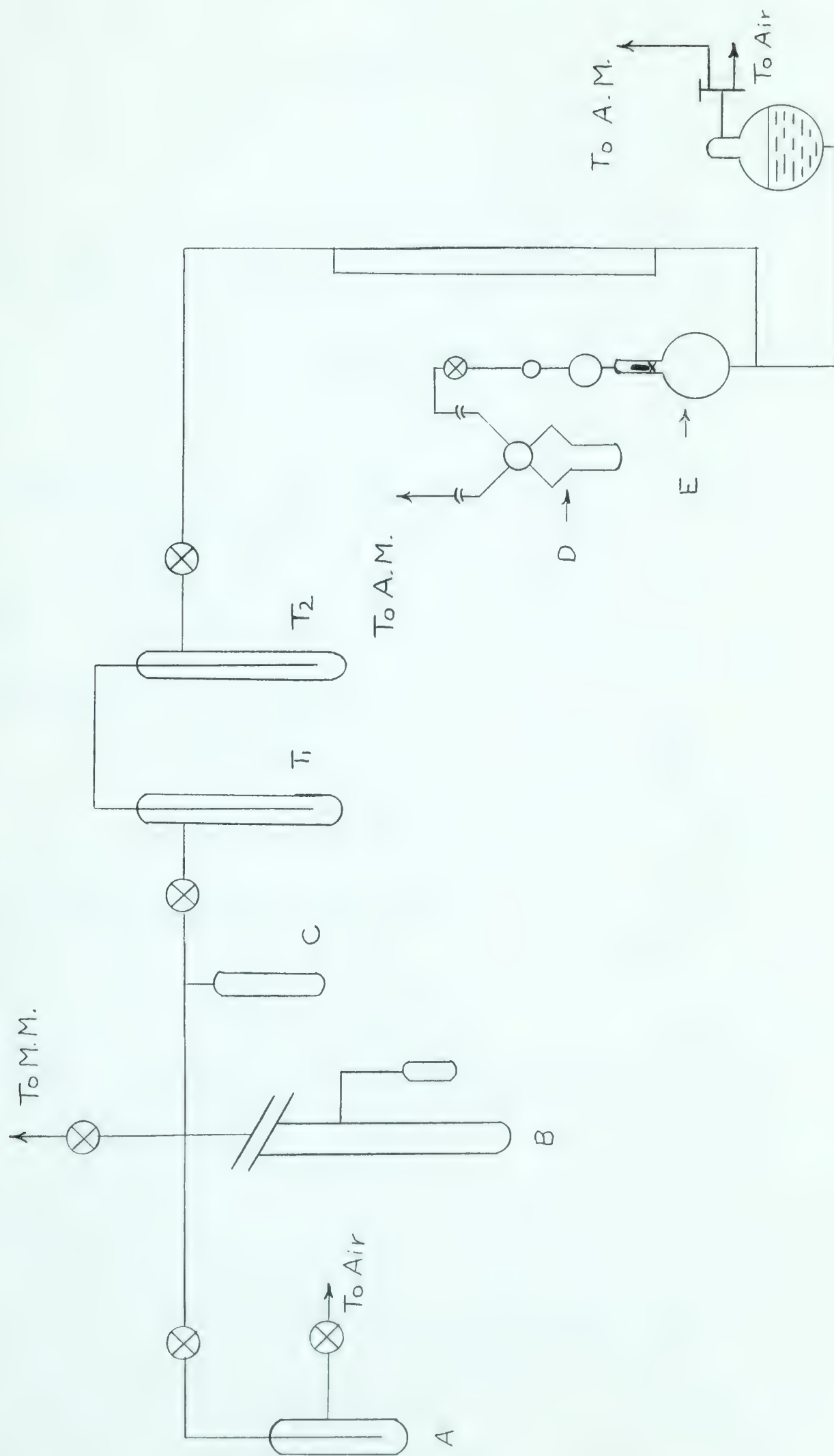





FIGURE II-8

## GAS ANALYSIS MANIFOLD FOR VAPOR PHASE SAMPLES.

(Not to Scale)

A	:	Cell into which the degassed sample is distilled and sealed off.
B	:	500 ml. bulb containing vapor phase sample.
C	:	"U" trap containing Molecular Sieve.
	:	Two Way Stopcock
	:	Ground Glass Joint
	:	14/20 Male Joint with breakseal at top
T <sub>1,2,3</sub>	:	Traps
T-McL.	:	Toepler-McLeod Gauge

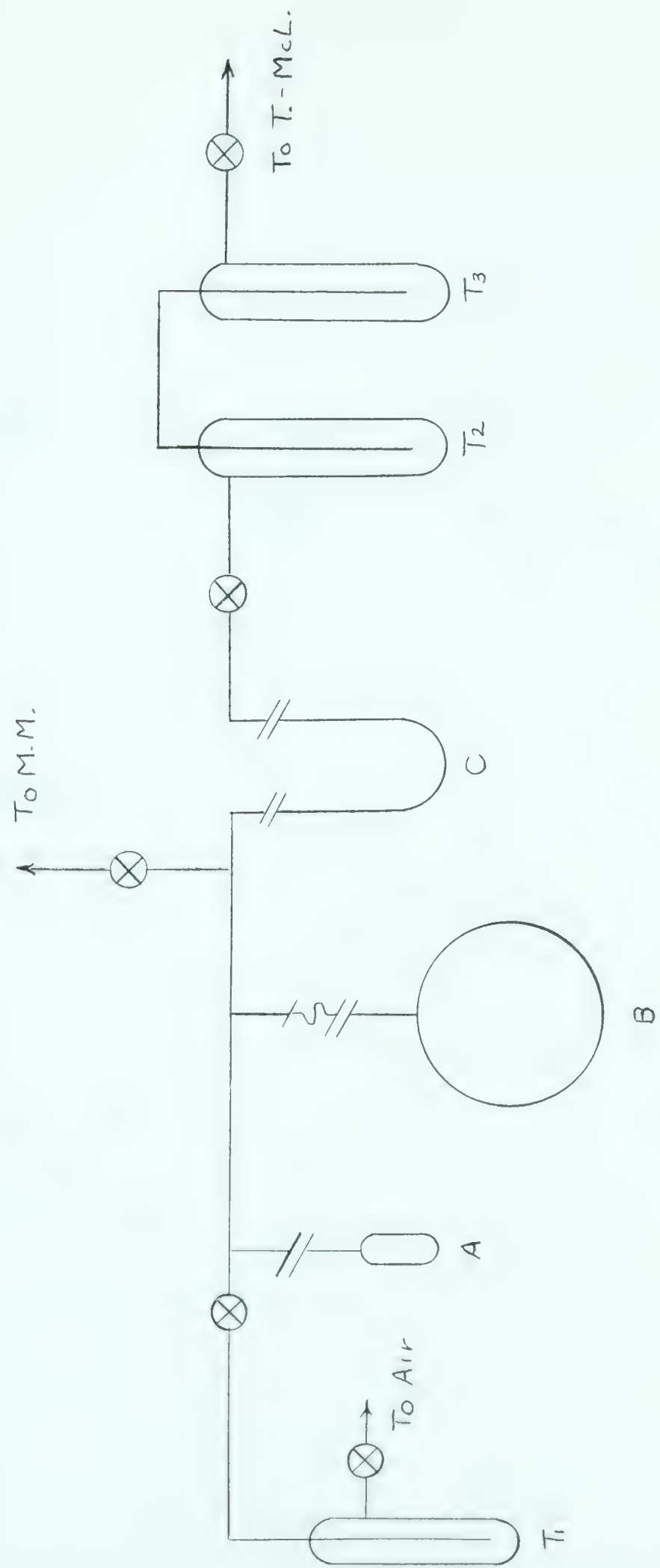
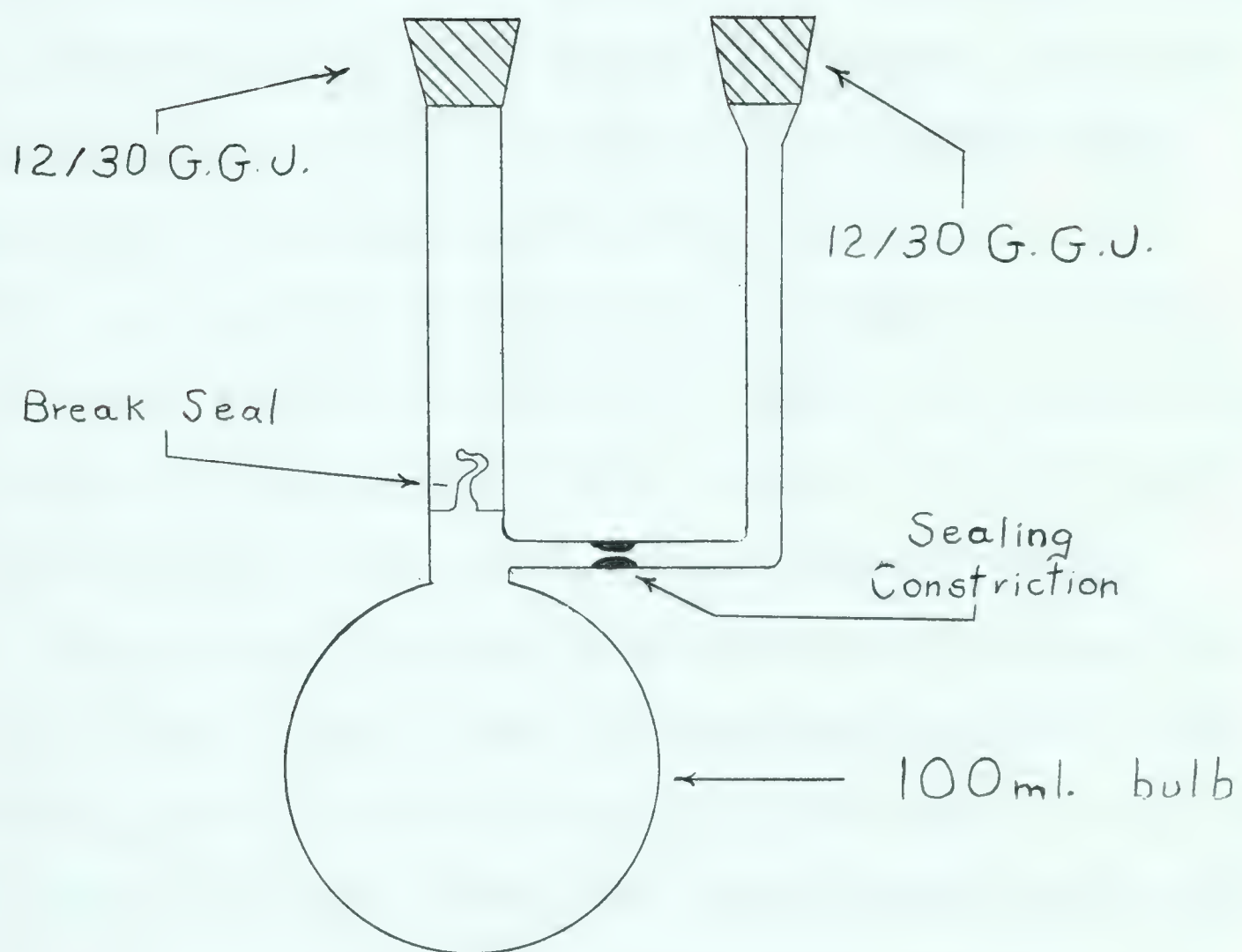


FIGURE II-9

GAS TRAP FOR MASS SPECTROMETRIC  
ANALYSIS.

(Not to Scale)

G.G.J.       :       Ground Glass Joint







b) Gas Chromatography.

Two types of gas chromatography (hereafter synonymous with (G.C.)) units were employed during the course of the investigations.

i. Burrell Unit.

The first was a Burrell model K-2 "Kromo Tog" which featured two detectors and columns with separate controls connected to one recording system. Two common types of flow system were employed. The "single stream" system's basic feature was that the same stream of gas flowed through both the reference and measuring sides of the detector. "Split stream" flow used two independent gas lines; one through the reference side and the other through the measuring side. Initial work with this instrument was done with single stream gas flow. However, most of the results were obtained with split stream which resulted in improved base line stability. The gas flow through one detector was as shown in Figure II-10. Helium carrier gas was used to obtain chromatograms of gaseous fractions, while hydrogen served as carrier for all liquid product analyses. Depending upon the partitioning column, the flow rate of carrier ranged from 50 to 125 ml. per minute. A burette bubble gauge measured the rate of flow. A combination of coarse and fine control needle valves (Edwards High Vacuum Ltd.) insured control of the flow rate to  $\pm 2\%$ . Purification of the carrier gas was accomplished by passing it first through a tube containing calcium chloride ( $E_1$  in Figure II-10) and then through a tube of Molecular Sieves ( $E_2$ ). From time to time,  $E_2$  was heated strongly with carrier flowing through it,



to restore its purification properties.

Two models of thermal conductivity detector cells (katharometers) were used. Initially, Burrell model 340-148 katharometers served to detect components in a sample. Later, model 340-149-01 was used. The latter cell featured replacable filaments and a higher sensitivity (2-4 fold) at the same detector current used with the earlier model. Normally, these detector cells were operated at a current of 200 mA while the cell bath was maintained at 200°C. Occasionally, different currents and bath temperatures served to give improved chromatograms.

The response of the detectors was displayed by a Brown-Honeywell Recorder model Y143X (full scale deflection 1 mv.).

ii. Gow-Mac Unit.

The other G.C. unit was constructed in the lab from individual components. The power supply was from Gow-Mac Instrument Co. (model 9999-C). The detector was a Gow-Mac model IR II-B temperature regulated thermal conductivity cell that used the same kind of replacable filaments as the Burrell detector model 340-149-01. The Gow-Mac detector was maintained at 200°C and operated at a current of 250 mA. The recorder for this chromatograph was from E. H. Sargent & Co., Model SR. A step-wise attenuator replaced the continuous one supplied with this recorder.

The flow arrangement for this second G.C. apparatus was essentially the same as that for the Kromo Tog. Split stream was used, the gas being purified by Drierite and Molecular Sieve tubes.





### iii. Separation Columns.

The columns used were of the "hair pin" type wound with a wire heating coil. The same columns could be used interchangeably on both Gow-Mac and Burrell instruments. Most columns were programmed from room temperature by applying a voltage to the heating coil while the column was surrounded by an insulating box. When the columns were connected to the Kromo Tog, a thermocouple measured the column temperature, which was read from a meter incorporated into the instrument. A Weston dial thermometer registered column temperature for the Gow-Mac apparatus.

Column lengths of 1 and 2.5 meters were employed. Silicone rubber seals from Burrell Corp. connected them to the inlet gas stream and the detector, and sealed the sample-injection and thermocouple ports.

Several solid supports and partitioning agents were tried to effect desired separations with varying degrees of success. A list of column packings and partitioning agents tested for possible product separation are given in Table II-3, page 58. Only six of these (marked \* in the first row of the table) were used to obtain quantitative results.

### iv. Water Analysis Arrangement.

Initial attempts at determining  $G(H_2O)$  were unsatisfactory, so a  $G$  .C. arrangement modified from the conventional Kromo Tog set-up was devised.

#### 1) Sample Crusher.

A sample bulb crusher was made by effecting certain alterations to a brass gas valve. The result is shown in Figure II-11(A). The sample

FIGURE II-10

## GAS CHROMATOGRAPHIC SYSTEM

(Not to Scale)

A	:	Cylinder of Eluent Gas
B	:	Gas Needle Valve
C	:	Gas Needle Valve
D	:	Fine Control Needle Valve
E <sub>1,2</sub>	:	Gas Purifying Tubes
F	:	Gas Sampling Device
G	:	Chromatographic Column
H	:	Bubble Type Flow Gauge

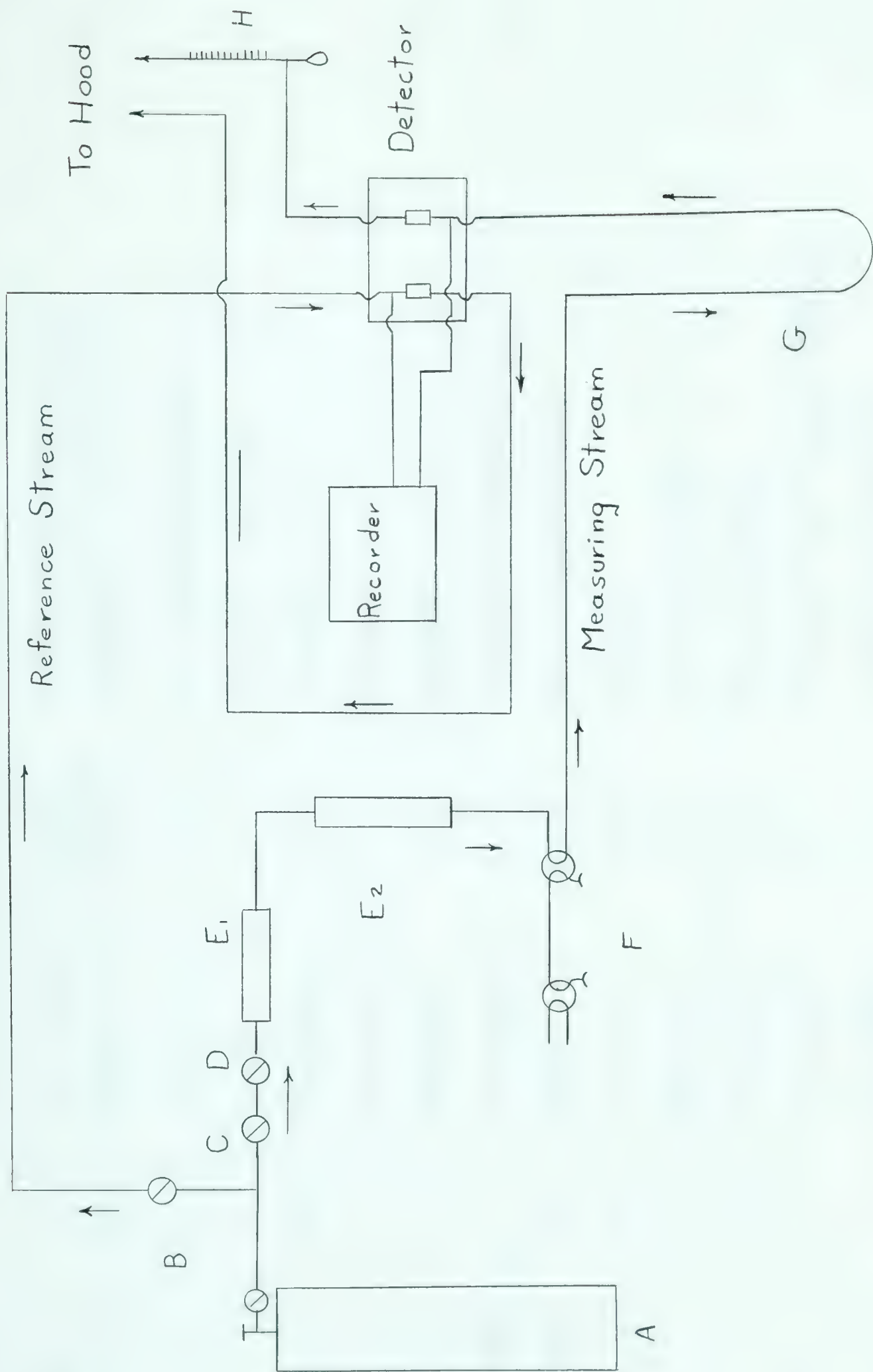




TABLE II-3

GAS CHROMATOGRAPHY COLUMNS.

Partitioning Agent	%	Solid Support	Length (meters)	Compounds to be Separated
Mannitol *	20	Celite	2.5	Glycols
Silica Gel *	--	-----	2.5	C <sub>2</sub> - C <sub>5</sub> Hydrocarbons
Charcoal *	--	-----	1	H <sub>2</sub> , air, CO, CH <sub>4</sub>
Ucon LB-1800X *	20	Firebrick	1	Glycols
Carbowax 4000	5	Fluoropak	2.5	Glycols
Octoil-S	5	Fluoropak	2.5	Glycols
Di-n-decyl phthalate *	5	Fluoropak	2.5	Glycols and Methanol
Di-n-decyl phthalate	15	Celite	2.5	Glycols and Methanol
Apiezon L	20	Firebrick	2.5	Glycols
Carbowax 4000	5	Fluoropak	2.5	Glycols and H <sub>2</sub> O
Carbowax 1540	5	Fluoropak	2.5	Glycols and H <sub>2</sub> O
Carbowax 1500 *	5	Fluoropak	2.5	Ethanol, H <sub>2</sub> O, Acetal, Methanol
Silicone Oil	5	Fluoropak	2.5	Ethanol and Methanol
Carbowax 20M	15	Celite	2.5	Ethanol, H <sub>2</sub> O and Acetal
Pluronic P84	5	Haloport F	2.5	Ethanol, H <sub>2</sub> O and Acetal





TABLE II-3 - Continued

Partitioning Agent	%	Solid Support	Length (meters)	Compounds to be Separated
Carbowax 6000	6	Halopart F	2.5	Ethanol, H <sub>2</sub> O and Acetal
Carbowax 4000, Stearate	1	Glass Beads	2.5	Ethanol, H <sub>2</sub> O and Acetal
THEED	4	Fluoropak	2.5	Ethanol, H <sub>2</sub> O and Acetal
THEED	25	Celite	2.5	Ethanol, H <sub>2</sub> O and Acetal
Silicone Oil 710	10	Firebrick	2.5	Ethanol, H <sub>2</sub> O and Acetal
Silicone Oil 710	8.5	Fluoropak	2.5	Ethanol, H <sub>2</sub> O and Acetal
Silicone Grease	35	Celite	2.5	Ethanol, H <sub>2</sub> O and Acetal
Tri-O-tolyl Phosphate	5	Fluoropak	2.5	Ethanol, H <sub>2</sub> O and Acetal

\* Used to obtain quantitative results.

## FIGURE II-11

## (A) SAMPLE CRUSHER FOR WATER ANALYSIS BY G. C.

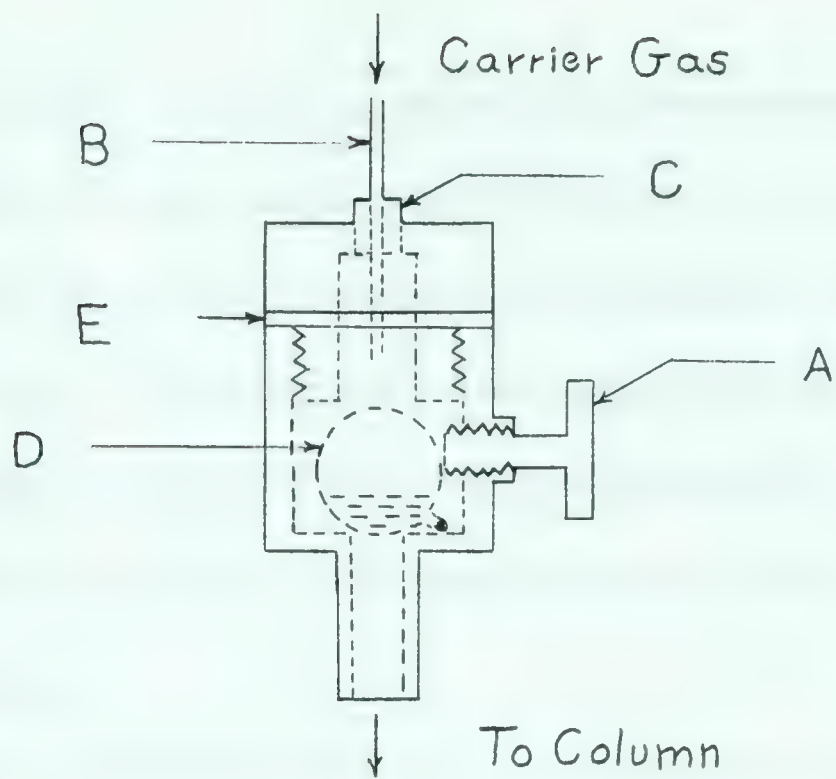
(Not to Scale)

A	:	Screw Type Breaking Rod
B	:	Capillary Steel Tubing
C	:	Silicone Rubber Seal
D	:	Sample to be Broken
E	:	Teflon Gasket

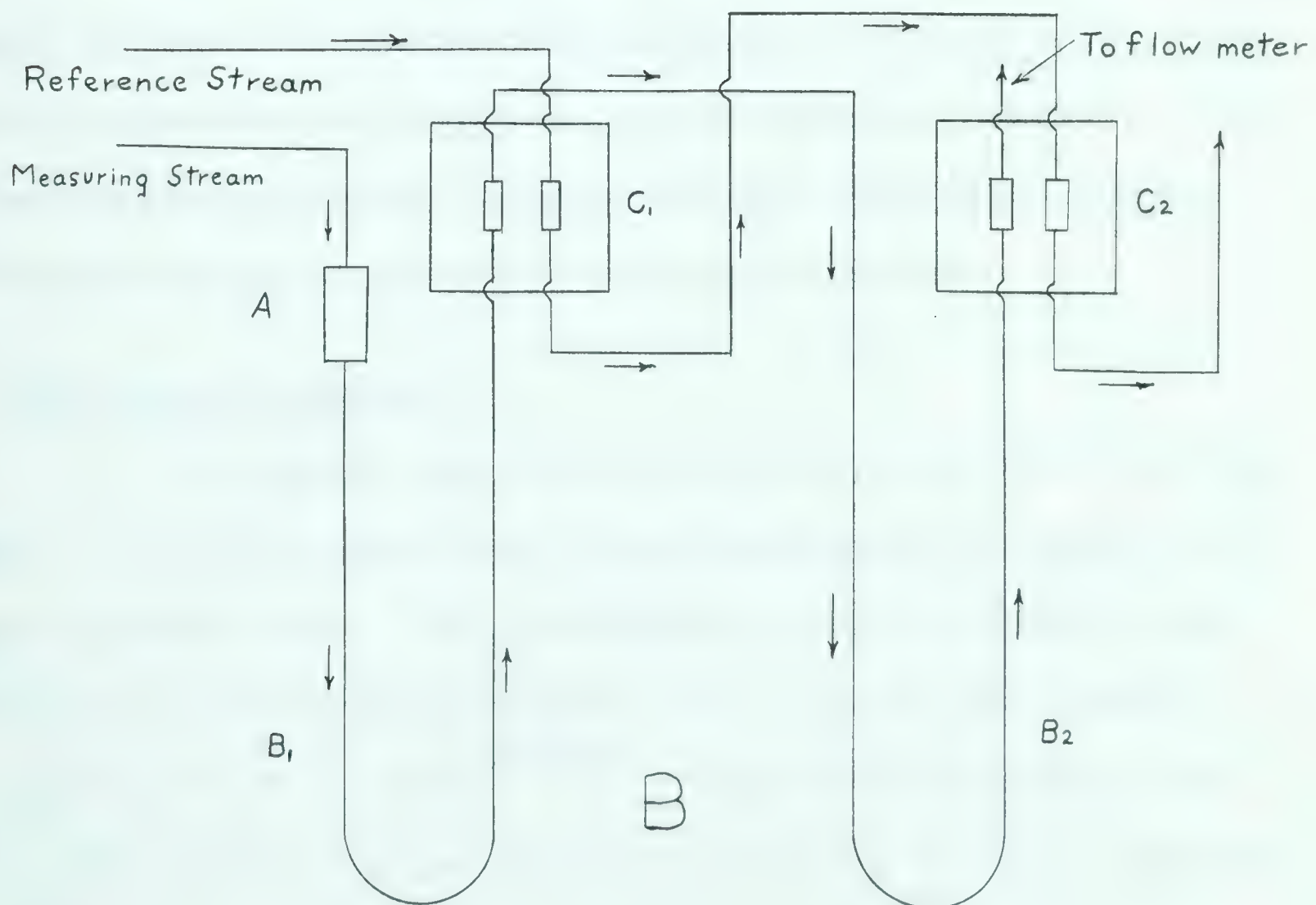
## (B) G. C. SYSTEM FOR WATER ANALYSIS.

(Not to Scale)

A	:	Sample Crusher of Figure II-11
B <sub>1</sub>	:	Carbowax 1500 on Fluoropak 2.5 column.
B <sub>2</sub>	:	n-Di-decyl phthalate on Fluoropak 2.5 meter column.
C <sub>1</sub> , C <sub>2</sub>	:	Thermal Conductivity Detector



A







was placed in the lower section and the upper section was screwed tightly into it. (A Teflon gasket provided a gas tight fit between the two sections.) Carrier gas entered the top section through a steel capillary tubing and silicone seal arrangement. Tight fitting Teflon tubing joined the column to the bottom of the breaker which sat directly on the sample inlet port. The whole of the breaker was wrapped in insulated electrical heating tape.

## 2) Analysis System.

Two columns and two detectors were necessary to obtain the desired analysis. The path of the carrier gas was as in Figure II-11(B). The sample crusher described above was placed at the inlet of the first column. After the sample had gone through the first detector it passed through a length of heated steel capillary tubing to the inlet of a second column where further separation occurred and was measured by a second detector. Both detectors were connected to a common recorder, which was switched to the second cell upon completion of the first chromatogram.

## c) Polarographic Apparatus.

Polarography was used to measure the product yield of acetaldehyde. Two polarographs (Leeds Northup Speedomax G Polarographs) were used at different times. The polarographic cell used in conjunction with these instruments is outlined in Figure II-12. The cell was originally designed by Dr. W. E. Harris<sup>(86)(87)</sup>. Figure II-12 and its legend were taken (with modifications) from the Ph.D. thesis of T. P. Jones, Chemistry Department, University of Alberta Figure 8, page 48.



A saturated calomel half cell served as the reference cell.

The cell vessel was a 25 ml. distillation flask to whose side arm was connected a length of flexible Tygon tubing terminating in a porous glass plug. The salt bridge made contact with the solution to be analyzed by means of the sintered glass tube C of Figure II-12. Electrical contact between the polarograph and the reference cell was effected by means of a copper wire dipping into mercury contained in a sealed 4 mm. O.D. soft glass tubing. Nichrome wire was sealed into this tube making contact with the mercury in the bottom of the calomel half cell vessel.

Electrolysis cells were constructed from 25 mm. O.D. Pyrex test tubes shortened to approximately 80 mm. length with flat bottoms. The height of all cells used was identical to  $\pm 2\%$ .

The dropping mercury electrode consisted of a mercury reservoir connected via flexible Tygon tubing to a very fine glass capillary tube (of approximately 130 mm. length) whose end was ground to a conical point. During a set of runs the height of the mercury column was kept constant and the capillary vertical to avoid altering the drop time of the electrode, which directly affects the diffusion current<sup>(88)</sup>.

To remove dissolved oxygen a stream of purified grade nitrogen (Canadian Liquid Air Co.) was passed through a bubbling tube into the solution to be analyzed. The bubbling tube terminated in a capillary tip to produce efficient purging action. All samples were de-oxygenated for identical times in a given set of samples as measured by a stopwatch (usually 50 seconds).

## FIGURE II-12

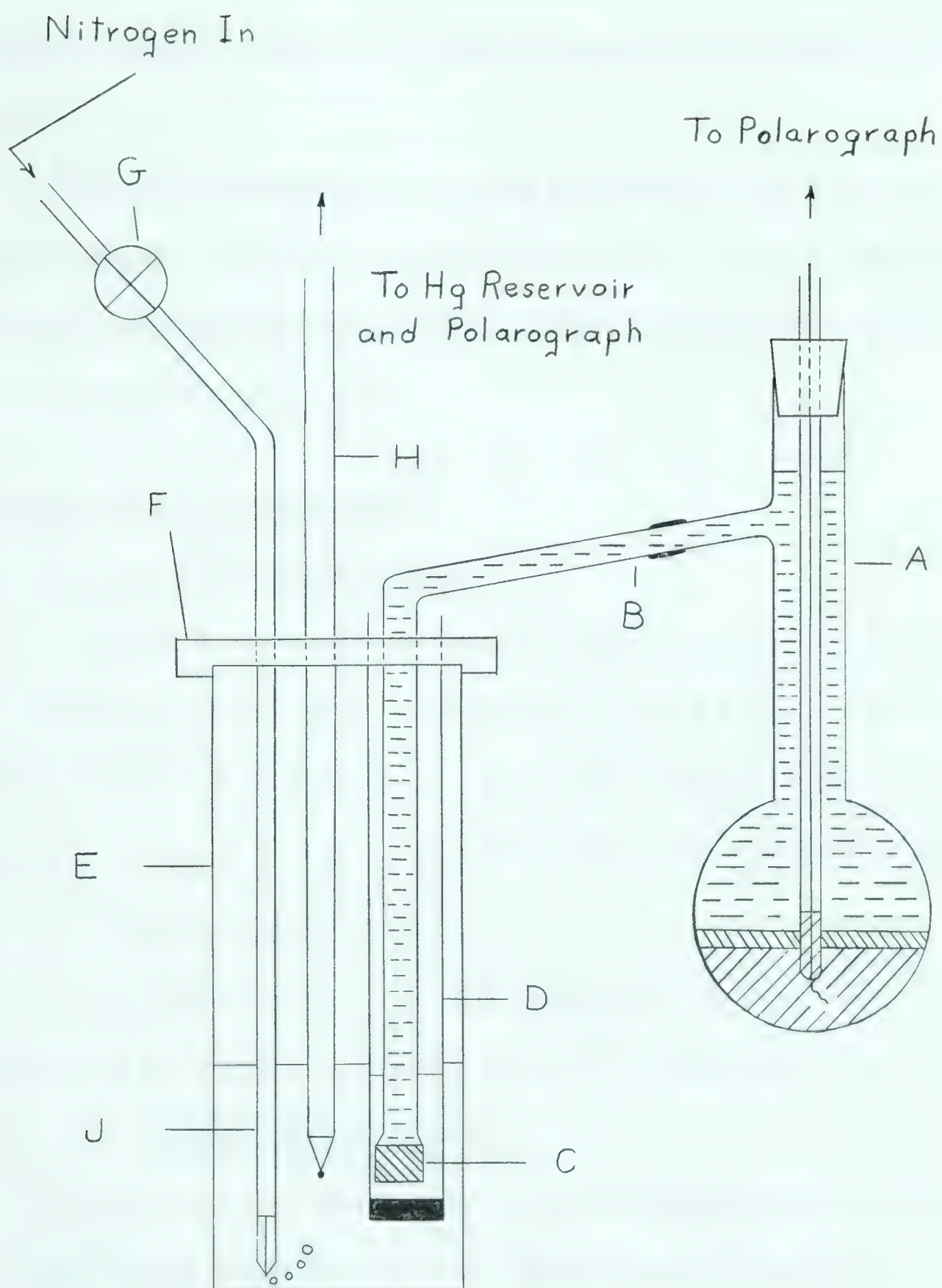
## POLAROGRAPH CELL

(Not to Scale)

Figure and legend modified from Figure 8, p. 48  
from Thesis of Thomas Jones, Chemistry Department,  
University of Alberta, 1961.

A	:	Saturated Calomel Half Cell
B	:	Flexible Salt Bridge
C	:	Porous Glass Plug
D	:	Sintered Glass Tube
E	:	Electrolysis Cell
F	:	3 Hole Polyethylene Lid
G	:	2 Way Stopcock
H	:	Dropping Mercury Electrode
J	:	Bubbling Tube









Electrolysis cells were always immersed in an ice-water bath in a Dewar flask. This flask was covered by a lid having apertures through which the electrolysis cell fitted to insure reproducible mercury column height etc.

The  $0^{\circ}\text{C}$  temperature bath was employed for two reasons. First, temperature control was greatly facilitated. Second, experiments using higher temperatures showed that a better polarographic wave was obtained for acetaldehyde at  $0^{\circ}\text{C}$ .

d) Other Analytical Instruments.

i) U.V. and I.R. Spectroscopy.

A Cary Recording Spectrophotometer model 14M was used for all ultra-violet analyses. For the dosimetry runs a 0.5 cm quartz cell was employed with air as reference. Infrared spectrographs for qualitative analysis were obtained with a Perkin-Elmer Infrared Spectrophotometer.

ii) Mass Spectrometry.

Mass spectrometry for both qualitative and quantitative purposes was done with a Metropolitan Vickers Model MS2 Mass Spectrometer.

iii) N.M.R. Spectrometry.

Qualitative and quantitative N.M.R. analyses were obtained using a Varian Associates Analytical N.M.R. Spectrometer Model A-60.

C. Procedures and Techniques.

a) Sample Preparation.



Samples were usually prepared in sets rather than individually, so a number of cells were connected at one time to the filling system. This minimized changes in vacuum conditions etc. between samples and made the blank (unirradiated) samples more representative of the actual state of the samples before radiolysis.

The glass used in the construction of the cells was chosen with reference to outside diameter, as the samples had to fit into the irradiation block with reasonably close tolerance. A poorly fitting sample could cause error in the calculated energy absorption. The tubing O.D. for ordinary liquid samples was approximately 15 mm. while the length was usually about 50 mm.. (Usually liquid samples were 1-2 ml. volume.) For short exposure runs a larger volume than usual of alcohol (10 ml.) was required, and the length of the cell increased accordingly.

Pyrex glass tubing used to fabricate the filling manifold, side arms and cells was given the following cleaning treatment. All glass was soaked in hot, freshly prepared sulphuric:nitric acid (5:2) cleaning solution for about 15 minutes. It was then washed 4 times with tap water. Next, it was twice rinsed with a dilute solution of sodium carbonate. Twelve rinsings with distilled water and four final rinsings with doubly distilled water (of the same purity as was used for dosimetry) completed the cleaning procedure.

Occasionally an extra few sample cells were intentionally not cleaned as rigorously as described above. Some of these samples that were analyzed for gaseous products showed  $G(H_2)$  to be considerably above that





usually measured. Small amounts of  $H^+$  have been shown to increase  $G(H_2)$  for liquid ethanol<sup>(45)</sup>. It is possible that traces of  $H^+$  remaining after acid cleaning were the cause of the high  $G(H_2)$  values. Hence, only the results obtained from samples whose cells had been cleaned according to the procedure outlined above were considered acceptable.

After the glass had been thoroughly cleaned, glass blowing to assemble the manifold and cells was done through a system that incorporated a silica gel breath filter.

The ethanol to be radiolysed was purified and stored in a Pyrex glass reservoir as described previously. Degassing was initially carried out by the freeze-pump-thaw method in the reservoir itself, utilizing a liquid nitrogen bath. Later, it was shown that improved blanks for the  $-112^\circ C$  gas fraction could be obtained by degassing the substrate at  $-112^\circ C$  (ethanol slush bath).

Before any samples were filled, the sample cells, side arms, and manifold tube were heated strongly while being pumped on, to remove adsorbed vapors. This procedure was continued until there was no deflection of the Pirani gauge upon heating the cell (usually two or three heatings were necessary). Then a small quantity of substrate was distilled into each sample tube to effect possible displacement of impurities on the glass walls. This "wash" substrate was subsequently pumped away through the main manifold. Immediately afterwards the samples were prepared as follows.

Determination of the quantity of ethanol radiolysed involved



volume measurements in tube C.T<sub>1</sub> of Figure II-2. The alcohol was distilled to this tube by cooling the tube intermittently with liquid nitrogen, with FV<sub>1</sub> of Figure II-2 open. An amount of ethanol slightly in excess of that required was transferred. This small excess was pumped away at 0°C, thereby effecting a further efficient degassing operation. (The high cost of the deuterated samples prevented this rather wasteful procedure.) An ice-water bath surrounded the measuring tube when the final volume reading was taken. Density tables from the 41<sup>st</sup> edition of the Handbook of Physics and Chemistry were used to calculate the weight of ethanol in the sample. For large volume (10 ml.) samples a second calibrated tube was attached to the system and the samples were measured by the same procedure.

When the amount of the ethanol had been accurately measured in the calibrated tube, it was distilled into the sample cell. After complete transferal, the sample was subjected to a final degassing in the cell. The sample cell was then sealed off at its neck while its main body (including all the substrate) was immersed in liquid nitrogen. Afterwards, the cell was maintained at -196°C until the section that was sealed cooled to room temperature. This waiting period helped to insure that no vaporized substrate was pyrolyzed at the hot section.

For all liquid ethanol samples, calculation showed that the amount of substrate present in the vapor phase in the measuring system at the prevailing temperature was negligible ( $<0.5\%$ ), compared to the volume of the liquid.





The irradiated samples were stored in a dark place up to the time of analysis to preclude the possible occurrence of photolytic reactions.

The first preparation of samples specifically designed for water analysis made use of essentially the same filling procedure as outlined above. The type of cell and sample volume, however, were quite different. Again the calibrated tube (C.T<sub>1</sub> of Figure II-12) measured the amount of alcohol; but due to the nature of its graduations the sample size had a possible error  $\pm 10\%$ .

A later set of runs for determining the yield of water produced from radiolysis involved pressure, volume, and temperature measurements of the alcohol contained in a two liter bulb (see Figure II-4(B)).

The ethanol reservoir was cooled to a point where its vapor pressure was low and then float valve F.V.2 was opened so that the ethanol, while warming, entered the bulb under its increasing vapor pressure. The pressure was allowed to increase to somewhat beyond that pre-calculated for proper sample size. Upon attaining the desired pressure, the measuring system and the reservoir were then isolated from each other. Volume calibration for this substrate measuring section had been carried out previously. By opening this portion of the vacuum line to the manifold containing the cells, the ethanol could be transferred quantitatively by cooling the cell in liquid nitrogen. In actual practice, it was found that complete transfer of the ethanol was very slow, presumably due to adherence of alcohol vapor to the walls of the two liter bulb. Hence, it was found to be more efficient to transfer approximately 90% of the substrate to the cell,





the exact amount being determined by initial and final pressure readings. These pressure readings were obtained from a mercury manometer incorporated into the system (using a Cathetometer capable of reading to  $\pm 0.05$  mm.). Again the liquid volume of substrate at room temperature was approximately 0.1 cc.

Substances deliberately added to the alcohol, to study possible inhibitory action were measured in various ways, dependent upon the amount and nature of the "inhibitor". When it was necessary to add 5% or less benzene, use was made of a special vessel (see Figure II-4(A)). Benzene was transferred to the vessel via a calibrated syringe. Immediately this container was affixed to the vacuum system and the benzene given preliminary degassing by the freeze-pump-thaw cycle. (Benzene loss by evaporation between volume measurement and connection of the vessel to the vacuum system was minimized by the small surface area of benzene exposed.) After initial degassing, the benzene was distilled to the sample cell, which already contained a measured amount of ethanol. Final out-gassing was done when the benzene and alcohol were mixed.

When larger amounts of benzene were to be added, it was measured by a second tube, C.T<sub>2</sub> of Figure II-2, calibrated in the same manner as C.T<sub>1</sub>; this tube was surrounded by a water bath of known temperature (approximately 15°C) when the volume was recorded.

As 1,3-pentadiene has a relatively high vapor pressure at room temperature, it was found advantageous to measure samples containing up to 20 electron % pentadiene by pressure, volume and temperature (PVT) readings



Above 20%, the total amount of diene was determined by adding the total amounts present as liquid in the measuring tube and as vapor in the volume above it.

Vapor phase irradiations were carried out in 500 ml. bulbs of the type shown in Figure II-3(C). The same cleaning procedure as was used for liquid samples was followed by irradiation of the bulbs filled with distilled water for a period of two hours. This pre-irradiation with water (to remove final traces of organic impurities) was used only for sample bulbs that were to contain alcohol without added "inhibitor". The bulbs for inhibited samples were given the acid-base-distilled water rinse without pre-irradiation. For washing, the bulbs were filled through the side arm while the break seal on the top of the bulb was open. After cleaning, the break seal was formed on top of the 14/20 cone by sealing and drawing the glass to the desired shape, (blowing into the bulb was avoided).

The bulb was then connected to the filling system via the 12/30 cone on the end of its side arm. (at G.G.J.1 of Figure II-2). After evacuation, the bulb and filling manifold were "flamed out" while being pumped on in the same manner as the liquid samples. The alcohol was then introduced into and measured in C.T<sub>1</sub> at 0°C. Complete transfer of this alcohol to the bulb and sealing at a constriction in its side arm completed the preparation.

Deuterated alcohol samples came from the manufacturer under vacuum in a Pyrex reservoir complete with breakseal. While being sealed into the system the alcohol was frozen at -196°C to avoid pyrolysis of its







vapor near the top of the reservoir. This reservoir was isolated from the rest of the vacuum system by a mercury float valve. When the measuring and filling systems were evacuated, the reservoir breakseal was opened by a magnetic plunger and the liquid was degassed at  $-112^{\circ}\text{C}$ . Four or five degassing cycles were usually necessary. Immediately afterwards, all samples of "pure" alcohol for irradiation and blank analyses were made up. Then 1,3-pentadiene mixtures with the alcohol in question were prepared.

Before a different deuterated compound was used for sample preparation, all the stopcocks that would come into contact with it at any time were removed, cleaned with carbon tetrachloride, regreased, and the system was re-evacuated for at least 24 hours.

The hydroxyl H or D atom in ethyl alcohol is capable of exchange. Therefore, before introducing  $\text{CH}_3\text{CH}_2\text{OD}$  and  $\text{CD}_3\text{CD}_2\text{OD}$  to the system from their reservoirs, all surfaces with which the alcohol would come into contact were pre-equilibrated with heavy water. Deuterium oxide of 99.84% isotopic purity was distilled into each cell to be filled and into the calibrated tube, in sufficient quantity that liquid  $\text{D}_2\text{O}$  was visible when the entire system was filled with heavy water vapor under its own vapor pressure at room temperature. After 20 minutes, the heavy water was pumped away and the system was flamed out by a hand torch. This process was repeated before the seal at the top of the alcohol reservoir was broken. N.M.R. analysis of "blank" samples taken after this treatment showed 99.9 % isotopic purity in the OD position for  $\text{CH}_3\text{CH}_2\text{OD}$  and 99.5% purity in  $\text{CD}_3\text{CD}_2\text{OD}$ . When an "OH" alcohol was used after an "OD" alcohol, again the stopcocks were cleaned and the system pre-equilibrated, this time with doubly distilled



light water.

b) Analysis of Gas Products.

i) (-196°C Gas Fraction)

After irradiation, liquid samples were placed thin bottom up, with an iron breaker in a 12 inch long trap (B in Figure II-7) attached to the analysis system via a 24/40 joint. The analysis system was then evacuated until three Toep lerings showed less than 0.2 microns as read by the McLeod gauge. Traps B,  $T_1$  and  $T_2$  were cooled in liquid nitrogen. After the stopcock to the main manifold had been closed, and periodic pressure checks by the McLeod gauge insured continued good vacuum, the thin sample bottom was broken by blows from the magnetic plunger. Toep lering of the gases volatile at -196°C (hydrogen, methane and carbon monoxide) was then begun. After 4-6 Toep lerings the liquid nitrogen was removed from trap B and the liquid distilled into  $T_1$  and  $T_2$ .

Analysis of the earlier sets of samples of 1 and 2 ml. showed that a second distillation at this temperature gave no observable increase in the gas measured. However, from time to time, an extra distillation at -196°C was effected to confirm this fact.

Vapor phase samples were treated in similar fashion. The sample bulb was connected to the system via a 14/20 cone joint with a break seal at the top. When vacuum conditions were suitable, the sample was opened to the rest of the system by breaking this seal. A single distillation at -196°C served to collect all the gas volatile at that temperature.





Due to the limited capacity of  $T_1$  and  $T_2$ , 10 ml. liquid samples could only be handled in this system by the inclusion of a side arm, C of Figure II-7. This side arm functioned as a third cold trap during gas collection. For these large volume runs a second distillation was necessary to completely collect the  $-196^\circ$  gas fraction.

Usually, after the  $-196^\circ$  gas fraction was measured, an aliquot of it was collected in one of the two types of gas traps of Figures II-6(B) and (C). This gas mixture was then analysed by gas chromatography.

For all gas phase samples and those liquid samples involving deuterated materials, the aliquot was collected in a vessel of the type depicted in Figure II-9. Before being sealed, the bulb was cooled to  $-196^\circ\text{C}$ . The contents of these bulbs were analysed by mass spectrometry. When a known mixture of  $\text{H}_2$  and  $\text{D}_2$  was sealed off in a bulb under the same conditions, no HD was detected by subsequent analysis. This fact showed that no significant "mixing" of the hydrogen was caused through pyrolysis at the hot sealed section.

For all sets of samples, at least one and usually two or more, blank unirradiated samples were put through the entire analytical procedure to detect, and if necessary correct for, insufficient degassing or poor vacuum during sample filling. For all results reported this correction was never significant.

#### ii) $-112^\circ\text{C}$ Gas Fraction

After the  $-196^\circ\text{C}$  fraction had been collected, the stopcock to the Toeppler-McLeod was closed and the sample was distilled to the side arm





of trap B (or for gas samples to ampoule A of Figure II-8). A "slush", made by adding liquid nitrogen to ethanol until it partly solidified (at a temperature of  $-112^{\circ}\text{C}$ ), was placed around the traps  $T_1$  and  $T_2$  and the sample was distilled to them while any gas at this temperature was collected in the McLeod gauge. At least two such distillations were carried out for all samples. For 10 ml. samples the side arm C of Figure II-7 was also maintained at  $-112^{\circ}\text{C}$ .

Pure alcohol samples gave a gas fraction consisting of ethane, ethylene, acetylene and propane. At very large irradiation doses a very small amount of butane was present.

When the ethanol slush was continually (after every two Toepferings) kept viscous by adding liquid nitrogen, no substrate escaped through the traps. This was shown by two distillations of blank samples at  $-112^{\circ}\text{C}$  which resulted in no or negligible pressure in the McLeod from ethanol or benzene. However 1,3-pentadiene has an appreciable vapor pressure at ethanol slush temperature and about 20% of this gas fraction from an irradiated sample consisted of diene.

In the earlier experiments, aliquots of the  $-112^{\circ}\text{C}$  fraction were analysed by gas chromatography. Later, the entire gas fraction was frozen into the appropriate gas sampler, by liquid nitrogen, and then analysed.

### iii) Liquid Products

After both gas fractions had been removed, the sample was distilled into the side arm cell of trap B or ampoule C of Figure II-7. During this final distillation, hot water (approximately  $80^{\circ}\text{C}$ ) was placed



around  $T_1$ ,  $T_2$  and the section of B that originally contained the sample. This was to insure that high boiling products (viz.  $C_2$ - $C_4$  glycols, whose boiling points are about  $200^\circ\text{C}$ ) reached the ampoule. The sample was then sealed for later liquid product analysis by polarography and gas chromatography. To determine whether any liquid products were lost during the gas analysis procedure, liquid products from a number of samples were measured without prior gas yield determination. Within experimental error, no difference in G value could be found.

c) Gas Chromatography.

i) Column Preparation and Conditions.

Column packings consisting of a partitioning agent upon a solid support were prepared by dissolving a weighed amount of the agent in a suitable solvent, mixing this solution with the solid support, and agitating the resultant "slurry" periodically until the solvent had evaporated. This resulted in a uniform coating of partitioning agent upon the solid support. The per cent composition of columns listed in Table II-3 are weight of separating material/100 gms. of inert support. Glass, "U" shaped columns of 1 or 2.5 m. length were filled with the appropriate packing and conditioned for at least 24 hours, at a temperature exceeding the maximum to be used for analysis.

Polar compounds, especially water, were found to "tail" badly using solid supports initially supplied with the Burrell instrument. Firebrick, Celite, Fluoropak 80, Haloport F, Teflon T6, and glass beads were







all tried as packing supports. Fluoropak 80 was shown to give chromatograms of polar compounds with the least tailing and was later used exclusively for all analyses involving liquid products.

Generally, gas samples were analysed by the Gow-Mac and liquid samples by the Burrell Chromatograph.

The conditions for the various columns employed for quantitative analysis are listed below together with the compounds separated.

#### Charcoal.

A 1 meter high activity charcoal column separated the compounds in the  $-196^{\circ}$  gas fraction. It was used at room temperature with a flow rate of 50 ml, per minute of helium carrier gas.

#### Silica Gel.

This separated the compounds in the  $-112^{\circ}\text{C}$  fraction. A flow of 50 ml. of helium per minute was used for this 2.5 meter column. It was temperature programmed from room temperature to  $100^{\circ}\text{C}$ .

The four columns below were operated with hydrogen as carrier gas.

#### Mannitol.

The 2.5 meter mannitol on Celite column was employed early in the investigation to determine G (vicinal glycol). The column was temperature programmed from room temperature to  $145^{\circ}\text{C}$ . while the carrier flow was 100 ml per minute.

#### Ucon LB 1800X

Ucon was a second column initially used to measure total vicinal



glycol. This 1 meter column with Firebrick support used a carrier flow of 90 ml. per minute and was programmed from room temperature to 150°C.

#### Carbowax 1500

Water analysis was always carried out with this 2.5 meter column, using Fluoropak support. Carrier flow was 100 ml. per minute. Programming from room temperature to 80°C gave best results.

#### Di-n-decyl Phthalate

This column was the only one found that could resolve a mixture of ethylene glycol, 1,2-propanediol, 2,3-butanediol and various other glycols in ethanol. It also measured acetal and sec-butyl alcohol. It was operated with a carrier flow of 125 ml. per minute and programmed to 140°C.

Measured column temperatures could vary from their true values by as much as 10°C (especially using the thermocouple-meter arrangement of the Kromo-Tog). However, reproducible temperature conditions were obtained by applying identical voltage settings to the heating coil of the column immediately after sample injection, for all samples.

It was found that the carrier gas flow was reduced as the column temperature increased during programming. For this reason, the flow rate listed previously for each column was measured while the column was at room temperature.

#### ii) Introduction of Samples.

Gas samples were introduced to the column by a sampling





device, to which a gas trap was connected by 12/2 ball and socket joints. The "side arms" of the trap were first "flushed out" by carrier gas. When the side arms were completely purged, initial conditions were restored and the aliquot was analysed.

Liquid samples were injected directly onto the column with a Hamilton micro-syringe. Injections were generally 100 microliters (100 $\mu$ ). Smaller amounts were sometimes used for special purposes. Greater amounts resulted in such a large parent (ethanol) peak that product peaks were obliterated. At least three injections on each column were made of each irradiated sample and the results were averaged.

iii) Blank Samples.

Along with each set of irradiated samples, "blanks" of ethanol (and ethanol-inhibitor solutions) were chromatographed. These could be used to correct peak areas and were useful in determining the base line for peaks that occurred on the "tail" of the substrate peak. At least three injections of each blank were made.

iv) Identification.

Identification of gaseous products was by their retention times on the appropriate columns. The limited number of possible gaseous products made this procedure definite in most cases. When there was any possible doubt (viz. propane) mass spectrometric analysis substantiated the identification from gas chromatographic retention time.

Liquid products were identified by their retention times on at least two columns. The acetal peak assignment was further proven by





trapping off of the peak from the di-n-decyl phthalate column and comparing its mass spectrometric cracking pattern with the pattern of a known sample of acetal.

v) Calibrations.

1) Gases.

Gas calibration samples were prepared as outlined in the Apparatus Section describing the gas sampling manifold. By filling the manifold to the appropriate pressure, successive samples could be taken from it without adding gas to the manifold between aliquots. All pressure readings were taken by means of a cathetometer capable of being read to 0.05 mm.

For all gases, except hydrogen, peak area was plotted versus pressure of gas in the sampler. For these gases, straight lines that went through the origin were obtained for pressures that were in the range of all irradiated samples. At considerably higher pressures of calibration gases, deviations from linearity were observed.

Hydrogen did not give a linear plot when treated in the same manner, due to the uniquely shaped peak obtained under the analysis conditions used. The peak height was measured rather than the area. At low pressures of hydrogen, a sharp positive peak increased in a non-linear fashion with pressure. Above a certain pressure, this peak height remained essentially constant while a very sharp negative peak (peak reversal) appeared that increased with pressure, in such a manner that it could be used to measure the amount of hydrogen in the sample. Plots of the hydrogen and



other gas calibrations will be given in the section dealing with results.

It was found that, over a period of time, the sensitivity of the detectors varied appreciably. Therefore, calibrations of hydrogen, methane and carbon monoxide were run during or immediately after each set of irradiations that involved their measurement. While the sensitivities of the  $C_2$  hydrocarbons also varied, their relative responses remained constant. Nevertheless, the major products in the  $-112^\circ C$  fraction (ethane and ethylene) were calibrated as frequently as hydrogen. Calibration factors for minor products were calculated from the relative responses determined at an earlier date.

## 2) Liquids.

The chromatograph was calibrated for liquids by solutions of the products in the substrate, prepared by weight. Four or five solutions of concentrations that spanned the range found in irradiated samples were measured. The substances to be calibrated were checked for purity by running a chromatogram of the pure substance. Appropriate corrections for impurities were applied to the solution concentrations.

Peak areas were measured by two methods. Usually the area was determined by the "peak height times half width" method. In some instances, however, the shapes of certain peaks were such that this method was not applicable and areas were measured by an Ott planimeter.

Peak areas was plotted versus concentration, expressed as molecules of the compound per gram of substrate, to give the calibration graph. The concentrations were calculated in this manner as the irradiation.





dose for samples to be analysed was expressed in e.v. per gm. of sample and hence G values could be calculated directly.

If the peak under consideration was well separated from the substrate peak, the calibration curve was usually linear and passed through the origin. When peaks appeared on the "tail" of the substrate peak non-linear plots sometimes were obtained.

Liquid calibrations were run with each set of samples requiring liquid product analysis.

#### d) Water Analysis.

The first attempts to obtain the value of  $G(H_2O)$  involved opening a sealed sample that had been previously subjected to gas analysis and injecting 100  $\lambda$  portions of it on the Carbowax 1500 on Fluoropak 80 column. The injections of aliquots of a sample were timed from the moment the cell was opened. Successive (five) injections showed a progressively larger water peak, even though the cell was tightly corked as much as possible. It was hoped that a plot of peak area versus time, extrapolated back to zero time, in conjunction with blanks treated in the same manner, would give a satisfactory measure of  $G(H_2O)$ . However, the results obtained were extremely scattered and were subsequently discarded.

Another set of irradiated samples and blanks were prepared in small thin bulbs which were crushed, in a sample crusher fabricated from pyrex glass, directly in the gas stream, again using the Carbowax 1500 column. The sample size was limited to 0.1 cc. of liquid, as larger amounts



"flooded" the column. Scatter was again a feature of the results.

Acetal was produced by reaction of the acetaldehyde with the ethanol in the sample and water was also a product of this reaction. Hence, both water and acetal were measured for the same sample using the small bulb technique. However, none of the columns listed in Table II-3 were capable of separating ethanol, acetal, and water from each other sufficiently well.

It was therefore necessary to devise a system using two columns to analyse one sample injection. The Carbowax 1500 column was used to separate ethanol and water. The sample then passed to a second column (di-n-decyl phthalate on Fluoropak 80) to effect ethanol-acetal separation. The flow system is shown schematically in Figure II-11(B).

The improved sample crusher of figure II-11(A) was wound with an insulated heating tape whose terminals were connected to a Variac voltage regulator. Before sample crushing, the sample was preheated to approximately 60°C.. This temperature was not measured accurately but temperature conditions from sample to sample were standardized by identical voltage settings. A "column blank" was then run to insure no water peak appeared due to temperature programming. Previous experience had shown that if the purifying tubes for the carrier gas were saturated, a significant water peak would show on the chromatogram by programming the column without injecting any sample on it. No measurable water peak from the carrier gas was observed during the water analysis for this last set of samples.





The stainless steel capillary tubing that led the sample from the first detector to the inlet of the second column was also wound with an insulated heating tape held in place by lengths of glass tubing. A Variac voltage setting maintained constant temperature conditions. The hydrogen carrier gas flowed through the two columns at a rate of 100 ml. per minute when measured with both columns at room temperature.

The preheated sample was broken by screwing a brass rod onto the bulb. It entered the Carbowax column, which was temperature programmed from room temperature, immediately after sample crushing by applying a voltage of 44 volts (maximum temperature approximately 70°C). The water peak emerged low on the tail of the ethanol peak. This chromatogram was continued for two minutes after the water peak had emerged in order to facilitate base line drawing for peak measurement. Then, at the same point for all samples (as measured from the crest of the alcohol peak by a stopwatch) the second column was temperature programmed from room temperature by a voltage setting of 56 volts (maximum temperature about 130°C). The recorder was immediately switched to the second detector which monitored the separation effected by the di-n-decyl phthalate column. Approximately one third of the alcohol had already passed through the second detector when the programming and recorder switching were started. The alcohol and acetal were well separated on this column. Failure to measure the complete alcohol peak on di-n-decyl phthalate was of no consequence as the acetal calibration and analysis were referred to the substrate peak measured from the Carbowax 1500 section of the chromatogram. A drawing of the type of





chromatogram obtained for a high irradiation dose sample is given in Figure II-13.

A repeated sequence of one blank followed by two irradiated samples was maintained during the analysis of the entire set of samples.

e) Polarography.

Acetaldehyde analysis by polarography was performed using the type of polarographic cell described in Figure II-12. A number of supporting electrolyte solutions<sup>(89)</sup> were tried, including (aqueous) 0.1M lithium chloride, 0.1M lithium hydroxide, and various mixtures of the chloride and hydroxide with a total concentration of 0.1M. Usually, the best acetaldehyde waves were obtained by using the 0.1M hydroxide.

Five ml. of the electrolyte and 0.5 ml. of the acetaldehyde containing solution were added to the cell, which was maintained at 0°C. After purging the cell contents of oxygen, at least four polarographic scans (usually two scans each at two different diffusion current attenuations) were run. After washing the gas bubbler, mercury capillary tube, and salt bridge with distilled water and drying them, four scans of a second aliquot of the sample were obtained. The average of these eight scans was taken as a measure of the acetaldehyde present. Aldehyde measurements for  $C_2H_5OD$  samples were done on a single aliquot due to the limited amount of the alcohol available. Blank solutions were treated to the same procedure as the irradiated samples. Calibration solutions spanning the concentration range of the irradiated samples were polarographed with each irradiated set. When diffusion current was plotted versus acetaldehyde

## FIGURE II-13

## CHROMATOGRAM FOR WATER AND ACETAL ANALYSIS.

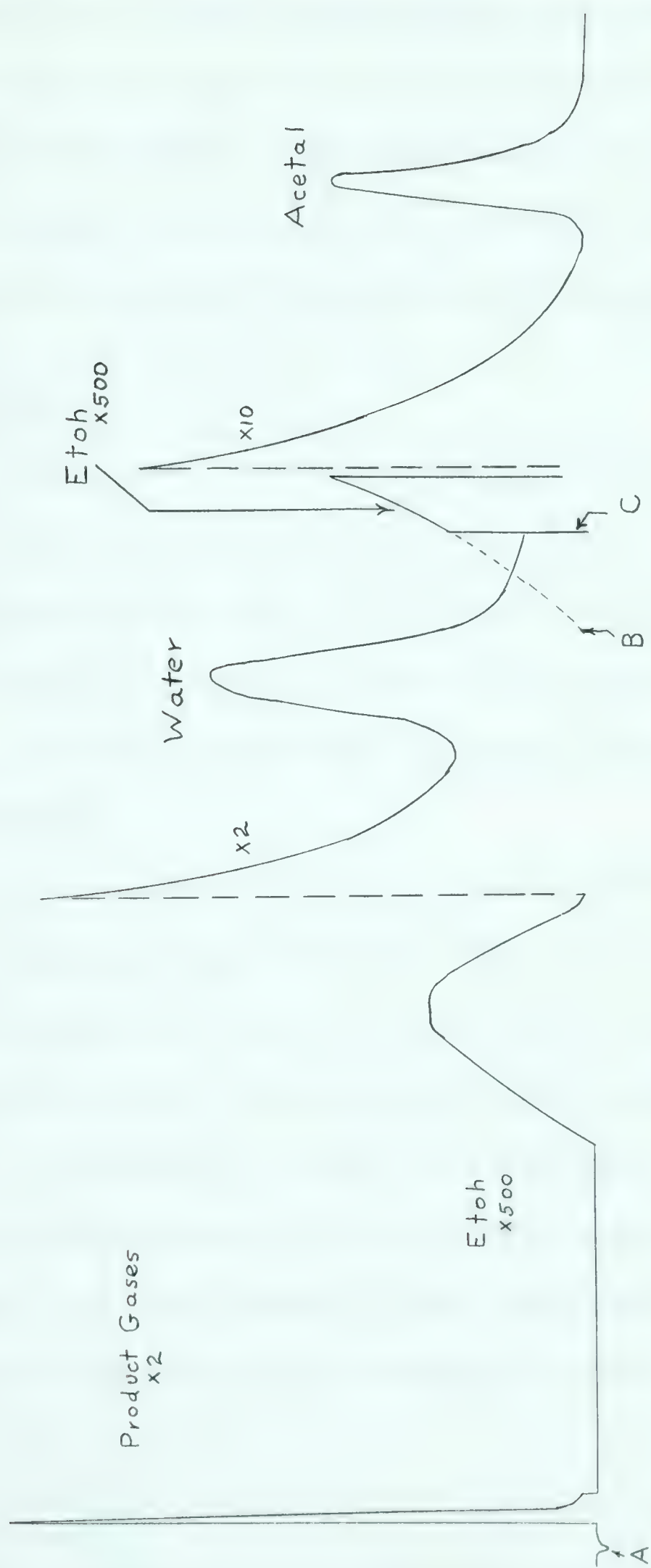
(approximately to scale)

Operating Conditions given on page 83.

- A : Sample introduced by crushing it
- B : Shape of the initial portion of the ethanol  
on DDP (missed by recorder)
- C : Recorder switched from detector having  
Carbowax column to detector with DDP  
column and attenuation varied.

DDP : di-n-decyl phthalate

|  
| : change of attenuation  
|







concentration, a straight line with zero intercept was obtained.

Due to the nature of the ill-defined acetaldehyde wave, special attention was paid to the analytical conditions to keep them invariant at all times. Consistency of technique was also essential to the actual measurement of waves from irradiated, blank and calibration solutions.

f) Mass Spectrometry.

It was found that the sensitivity of the mass spectrometer toward the gases introduced into it varied from day to day. Therefore, the compositions of the gas fractions from all samples for a given deuterated alcohol were determined by mass spectrometry with no waiting period between analyses. Sensitivity calibrations for product gases were run with each set of samples.

Four types of samples from each alcohol were irradiated and analysed; pure liquid, pure gas, inhibited liquid and inhibited gas. Previous light alcohol samples, whose results served to compare the results of light and the various heavy alcohols, had been analysed by gas chromatography. Consequently, a further set of light alcohol samples were irradiated at the same period as the deuterated compounds. The product gases from these were analysed by mass spectrometry to act as "control" runs and to establish analysis technique and conditions for the deuterated analyses.

HD for the  $-196^{\circ}$  calibrations was generated by passing the discharge from a Tesla coil for 12 hours through a mixture of  $H_2$  and  $D_2$  contained in a Pyrex bulb. The sensitivities of  $H_2$  and  $D_2$  were first deter-



mined from separate pure samples of each. (Sensitivities were expressed as peak height in cms. per micron of gas.) A mass spectrogram of a known pressure of the  $H_2$ , HD, and  $D_2$  mixture was then obtained. From the sensitivities of  $H_2$  and  $D_2$  the amounts of these gases present in the mixture were calculated and hence the sensitivity of HD could be found from its peak height and its pressure, as obtained by difference.

The  $-112^\circ C$  fraction for the light alcohol samples could be analysed completely from their "cracking patterns" at 75 e.v. bombardment energy. However the proper standard gases necessary to calibrate for partially and completely deuterated compounds were not available. Therefore, information concerning the composition of the  $-112^\circ$  gas fraction for deuterated alcohols was obtained from low voltage scans (in the range of 10-15 e.v.).

#### g) Formaldehyde Analysis.

Quantitative analysis for formaldehyde was carried out by a modified procedure of Eegriwe<sup>(90)</sup>. This procedure was capable of analysing solutions of formaldehyde in ethanol in the concentration range  $10^{-4}$  to  $10^{-1}$  M. Each analysis involved five samples (two irradiated, one blank and two standard formaldehyde solutions). The two standard solutions were of such concentrations that one was of lower and one of higher concentration than that expected from the irradiated samples. These concentrations were precalculated, using a value for  $G(HCHO)$  previously determined<sup>(17)</sup> and the dose received by the irradiated samples.





Five 10 ml. Erlenmeyer flasks served as the sample containers and  $110 \pm 1$  mg. of chromotropic acid was weighed into each. Then 0.8 ml. of doubly distilled water and 0.20 ml. of the solution to be analysed (blank, irradiated sample or standard) were added. The resulting solutions were evaporated to dryness, together, by heating them exactly 25 minutes in an oil bath maintained at  $110 \pm 2^\circ\text{C}$ . After cooling them to room temperature, 5.0 ml. of concentrated sulphuric acid was added to each flask. These acid solutions were heated in the oil bath for exactly 30 minutes at  $130 \pm 2^\circ\text{C}$ . Then the flasks were removed from the oil bath and again cooled to room temperature. The solutions were transferred to larger glass stoppered flasks and 15.0 ml. of doubly distilled water was added to each. Again the solutions were cooled and the optical densities of the solutions at 570 m $\mu$  was measured. This was done as quickly as possible and the solutions were never allowed to stand more than one hour before optical density measurements were taken.

The standard solutions were prepared from aqueous formaldehyde solution with a label analysis of 36.6% formaldehyde by Fischer Scientific Co. This analysis was checked by the dimedon (methone) procedure taken from Shriner and Fuson<sup>(91)</sup> and  $G(\text{HCHO})$  for the samples was corrected accordingly.

#### D. Irradiation.

##### a) Sources.

All samples were irradiated by  $\text{Co}^{60}$  gamma rays. Over the





course of the investigations three different  $\text{Co}^{60}$  sources were employed. These units and their characteristics are briefly described below.

i) Cancer Therapy Unit.

The initial irradiations made use of the therapeutic  $\text{Co}^{60}$  unit of the Government of Alberta Cancer Clinic at the University Hospital. A Lucite block, into which holes of the appropriate size were drilled, served as the sample holder. The sample cells fitted into these holes with close tolerance and the block was placed reproducibly in the beam collimator of the unit.

The sample holding block was a considerable distance from the cobalt source itself and the dose rate for the sample positions ranged from approximately  $0.6 - 1.0 \times 10^{18}$  e.v./ml. of  $0.8\text{N H}_2\text{SO}_4$  — hour. The geometry of the arrangement was such that the dose rate was independent of sample size in the range employed (1.0 - 2.0 ml.). Irradiations were performed at a temperature of  $25^\circ\text{C} \pm 2^\circ\text{C}$  with this source.

ii) Cobalt "Bomb".

The second source (referred to as the "bomb") was essentially a cobalt capsule that was housed in a large steel and lead case. Both the  $\text{cobalt}^{60}$  source and its surrounding case were constructed by the Atomic Energy of Canada Ltd. This unit was housed in a thick walled room (cave) adjoining the laboratory. The connecting passage between the two rooms contained a number of right angle bends to minimize the background of deflected gamma rays. The source was operated by remote control from the laboratory.



Sample holders similar to the one utilized with the Cancer therapy unit were placed in reproducible positions close to the source. (Slight modification of the blocks was necessary for small bulb samples.)

This arrangement permitted dose rates up to  $8 \times 10^{18}$  e.v./ml. of 0.8N  $\text{H}_2\text{SO}_4$ -hour to be obtained.

The temperature of the irradiation room was measured before and after irradiation and was always  $25 \pm 4^\circ\text{C}$ .

iii) Gammacell.

Gas phase and all deuterated alcohol radiolyses (including the control runs with light ethanol) were performed using a Gammacell 220 Cobalt Irradiation Unit obtained from the Atomic Energy of Canada Ltd.

Essentially, the unit consisted of (92) an annular shaped source, a lead shield around the source and a long cylindrical drawer free to move vertically through the centre of the source.

The dose rate was  $6 \times 10^{19}$  e.v./ml. of 0.8N  $\text{H}_2\text{SO}_4$ -hour.

The holder for liquid samples for the Gammacell consisted of an aluminum "can", around whose perimeter holes were bored to receive the samples. As in the previous irradiation arrangements, reproducibility of sample position was strictly observed.

Due to the intensity of the gamma ray flux from this source temperature control for liquid samples was a greater problem than with previous sources. Therefore, a circulating water bath was utilized to maintain the temperature during irradiation to  $26 \pm 3^\circ\text{C}$ .

Gaseous samples were contained in 500 ml. bulbs, of which only





one could be irradiated at any given time.

The gas sample (prepared as described previously) was maintained in the vapor state by completely enclosing the bulb, its neck, break-seal, and sealed off side arm in a heating mantle fabricated from an insulated electrical heating tape. The sample and surrounding mantle were placed in a metal frame in the sample drawer. The terminals of the heating mantle were connected to a Variac by which the heat supplying current could be controlled. Measurement of the sample temperature was accomplished by means of an iron-constantan thermocouple whose probe was knitted into the mantle and rested against the Pyrex walls of the bulb.

Gas phase samples were always preheated to the temperature to be maintained during irradiation. When this temperature ( $105 \pm 3^\circ\text{C}$ ) was achieved, and maintained, the sample was exposed to the gamma rays by lowering the sample drawer into position inside the source cage.

#### b) Dosimetry.

Dosimetry (the quantitative measurement of the energy absorbed by a sample) was accomplished by chemical means.

##### i) Liquid Sample Dosimetry.

Liquid phase dosimetry utilized the Fricke dosimeter<sup>(93)</sup>. Energy absorption calculations were based on  $G(\text{Fe}^{++}) = 15.5^{(93)}$  and  $\epsilon(\text{Fe}^{++})$  at  $304 \text{ m}\mu = 2225 \text{ liter mole}^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}^{(94)}$ . Dose rates for all irradiations were corrected for the radioactive decay of the  $\text{Co}^{60}$  (half-life



$=5.28 \text{ years})^{(95)}$ .

Dose rate measurements for the therapy unit were taken from data of Dr. G. R. Freeman in June 1959.

Dosimetry for liquid samples involving the use of the "bomb" was performed using a variety of sample sizes (0.4 - 10.0 ml.) for the block positions used. A graph of measured dose rate was plotted versus sample volume and the dosimetry for the water analysis samples (0.1 ml. volume) was obtained by extrapolation.

Gamma cell measurements were obtained for 1 ml. samples only.

## ii) Gas Sample Dosimetry.

Ethylene radiolysis ( employing Phillips Research Grade substrate) served as the vapor phase dosimeter , using  $G(H_2)=1.28^{(96)}$ . The ethylene samples required a slight modification of the gas analysis system. It was found that the two cold traps , normally used during gas analysis , when kept at  $-196^\circ\text{C}$  did not hold back all the undecomposed ethylene from the Toepler-McLeod gauge . Therefore , a "U" trap filled with Molecular Sieves , immersed in liquid nitrogen , was incorporated into the system. This decreased the amount of ethylene escaping to the McLeod; however , the gas collected was analysed by gas chromatography utilizing a silica gel column. In some cases a significant correction had to be applied to determine the amount of hydrogen produced.

The dose rate was expressed as e.v./hour-gm of ethylene. For the various ethylene samples a plot of molecules of hydrogen evolved per gm.





of ethylene versus time gave a straight line through the origin.

The average of two sets of dosimetry runs performed, independently, by the author and a co-worker were used for dose rate calculations.

The energy absorbed by a gas phase sample is dependent upon the electron stopping power of the medium<sup>(96)</sup>. Stopping power ratios for ethylene and ethanol (and ethanol-inhibitor solutions) were calculated from the Bethe equation<sup>(97)(98)</sup>. This correction amounted to 1% which was less than the uncertainty of the ethylene dosimetry ( $\pm 5\%$ ).





## RESULTS

### (A) LIQUID ETHANOL .

#### a) Gaseous Products.

##### i) Gas Fraction volatile at $-196^{\circ}\text{C}$ .

The products comprising the  $-196^{\circ}$  fraction (hydrogen, methane, and carbon monoxide) were analysed, almost exclusively, by gas chromatography. The only exceptions were "control" samples of light ethanol for the deuterated ethanol samples. Results for the  $-196^{\circ}$  fraction obtained by both methods agreed within experimental error.

To determine the individual G values for the component gases by gas chromatography, an aliquot was analysed on a charcoal column. Amounts of each gas present in the aliquot were read from a series of calibration curves. The total  $G(-196^{\circ})$  was partitioned in accordance with the per cent composition found.

The sensitivity of the thermal conductivity detector cells changed appreciably over a period of time, although the relative responses of most gases remained essentially constant at the same detector current. However, hydrogen did not exhibit a linear calibration plot (pressure versus peak height), and thus frequent calibration for hydrogen, and at least one more of either methane or carbon monoxide, were carried out. A sample hydrogen peak height versus pressure plot is given in Figure III-1. Representative calibrations for methane and carbon monoxide are given in Figures III-2(A) and (B). The values used for these plots are presented in



Tables III-1 and III-2. Figure III-1 demonstrates the unique behavior of the hydrogen peak with increasing pressure in the gas sampler.

Many of the points on the methane and carbon monoxide calibration graphs correspond to pressures greater than those actually encountered in irradiated samples. However, they aided in establishing the slope of the lines and, as the intercepts were zero, the sensitivities could be used down to the smallest measurable peaks.

### Hydrogen

Hydrogen was the product obtained in greatest amount from the radiolysis of liquid ethanol. The yield of hydrogen as a function of dose is given in Figure III-3 and Table III-3. Over most of the range investigated,  $G(H_2)$  showed a slight decrease with increasing dose. At very low conversions there was a definite upward trend as the dose was reduced. The lowest dose sample values are shown on an expanded scale in the top half of the figure.

The values exhibited in Figure III-3 were obtained at three different dose rates, (approximately  $0.9$ ,  $5$  and  $60 \times 10^{18}$  e.v./gm. of ethanol - hour). Within experimental error, these three different dose rates generated the same quantity of hydrogen for a given dose.

Samples containing  $0.2\%$  and  $0.005\%$  water also gave the same  $G(H_2)$ , within experimental error.

The lowest dose samples had a volume of 10 ml. Due to the geometry of the source and the sample positions used, the same dosimetry

## FIGURE III-1

REPRESENTATIVE GAS CHROMATOGRAPHIC HYDROGEN  
CALIBRATION.

## Conditions:

Gow-Mac Apparatus

Detector Current 300 ma.

Charcoal Column

Helium Carrier Gas

Flow Rate 72 ml. of carrier/minute

Column maintained at room temperature ( $25 \pm 3^{\circ}\text{C}$ )  
during analysisCell Temperature  $400^{\circ}\text{F}$ 

- - - - -

Peak height units are 1/50 inch.



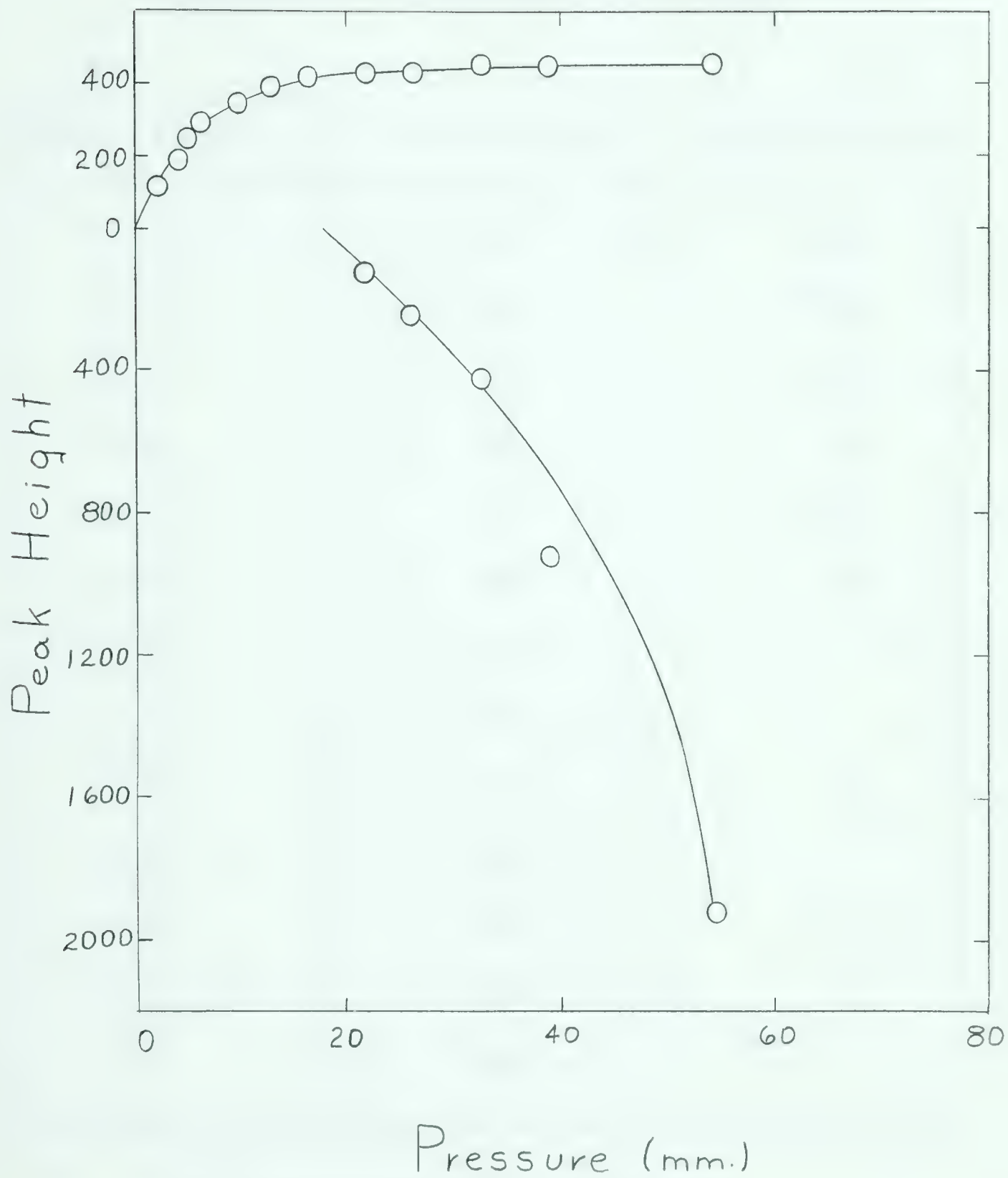




TABLE III - 1

## HYDROGEN CALIBRATION

(Peak Height versus Pressure in Sampler)

Pressure (mm.)	Positive Height	Negative Height
70.5	482	3650
54.4	453	1920
38.8	443	925
32.4	452	426
26.1	424	246
21.9	424	134
16.5	416	
12.9	387	
9.9	347	
6.6	292	
5.1	242	
4.2	192	
2.4	114	

Peak Height Units are 1/50 of an inch.

FIGURE III-2

REPRESENTATIVE GAS CHROMATOGRAPHIC CALIBRATIONS.

A.            Carbon Monoxide

B.            Methane

Same conditions as for hydrogen calibration for both plots.

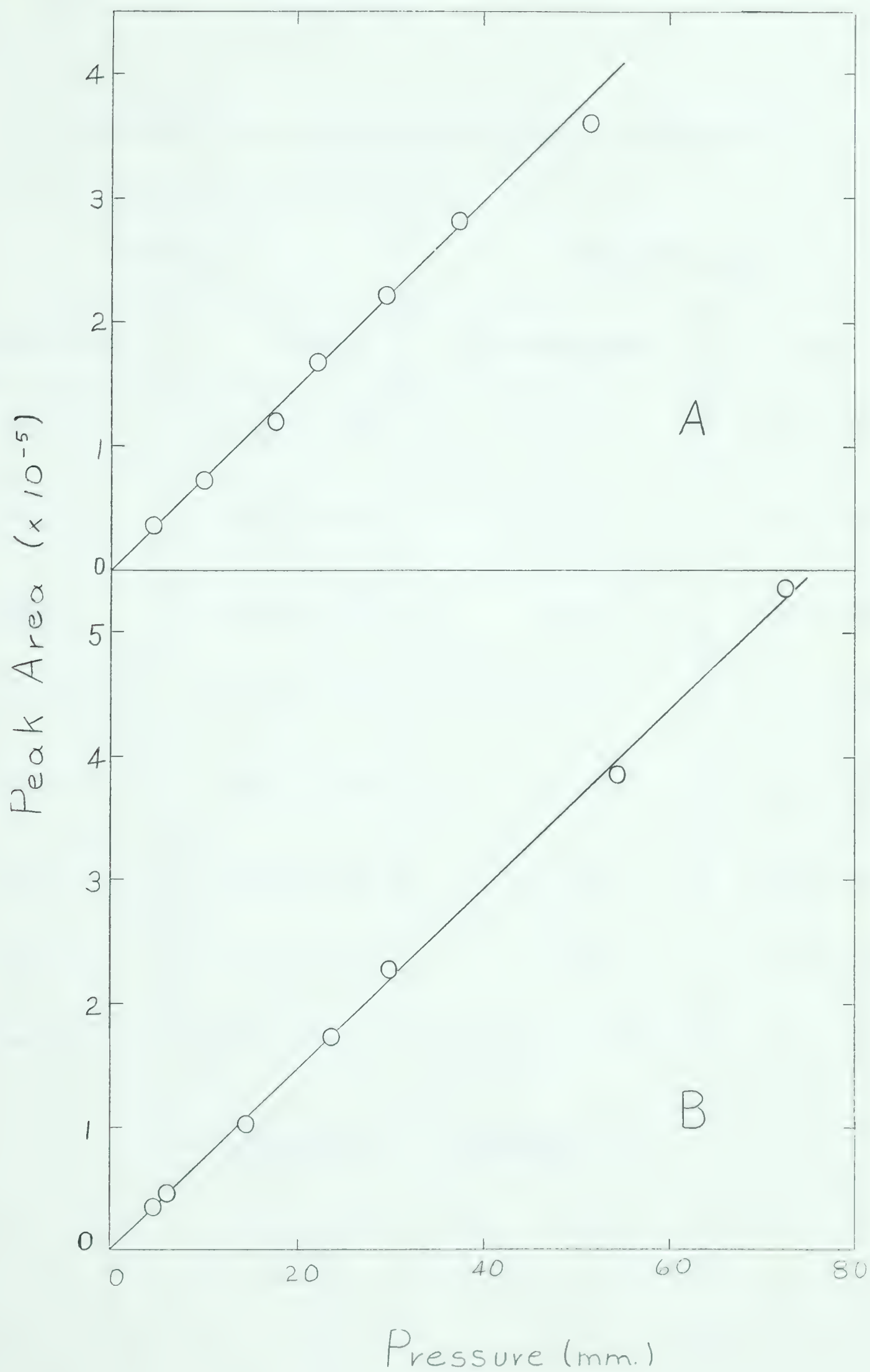






TABLE III - 2

## METHANE AND CARBON MONOXIDE CALIBRATIONS.

Methane		Carbon Monoxide	
Pressure (mm.)	Area*	Pressure (mm.)	Area*
72.5	$5.38 \times 10^5$	51.4	$3.62 \times 10^5$
54.6	$3.86 \times 10^5$	37.5	$2.80 \times 10^5$
30.0	$2.28 \times 10^5$	29.4	$2.22 \times 10^5$
23.4	$1.73 \times 10^5$	21.9	$1.67 \times 10^5$
14.4	$1.01 \times 10^5$	17.7	$1.20 \times 10^5$
6.0	$0.475 \times 10^5$	9.9	$0.73 \times 10^5$
4.5	$0.36 \times 10^5$	3.9	$0.35 \times 10^5$

\* 1 Area Unit  $\approx$  1/2500 sq. in.

## FIGURE III-3

## HYDROGEN YIELD AS A FUNCTION OF DOSE.

(Liquid Ethanol Radiolysis)

## A. Low Dose Samples

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm. of ethanol-hour; $H_2O$  content = 0.005%

Average of three values

## B. Normal Dose Range Samples



Taken from Plot A (above)

Dose Rate  $\approx 0.9 \times 10^{18}$  e.v./gm. of ethanol-hour; $H_2O$  content = 0.2%Dose Rate  $\approx 0.9 \times 10^{18}$  e.v./gm. of ethanol-hour; $H_2O$  content 0.005%Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm. of ethanol-hour; $H_2O$  content 0.005%

Average of 4 values at 3 different dose rates

(0.9, 5 and  $60 \times 10^{18}$  e.v./gm.-hour)

(see Table III-1)

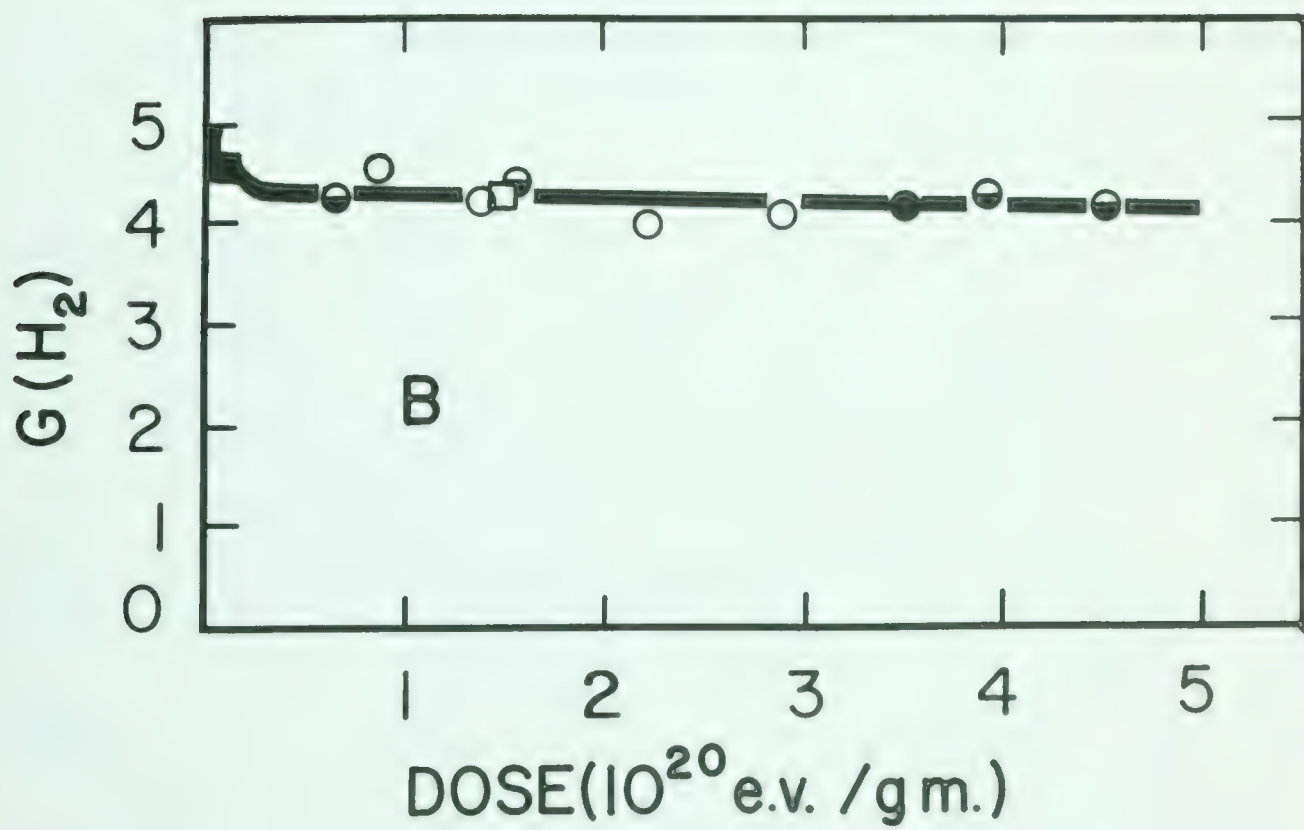
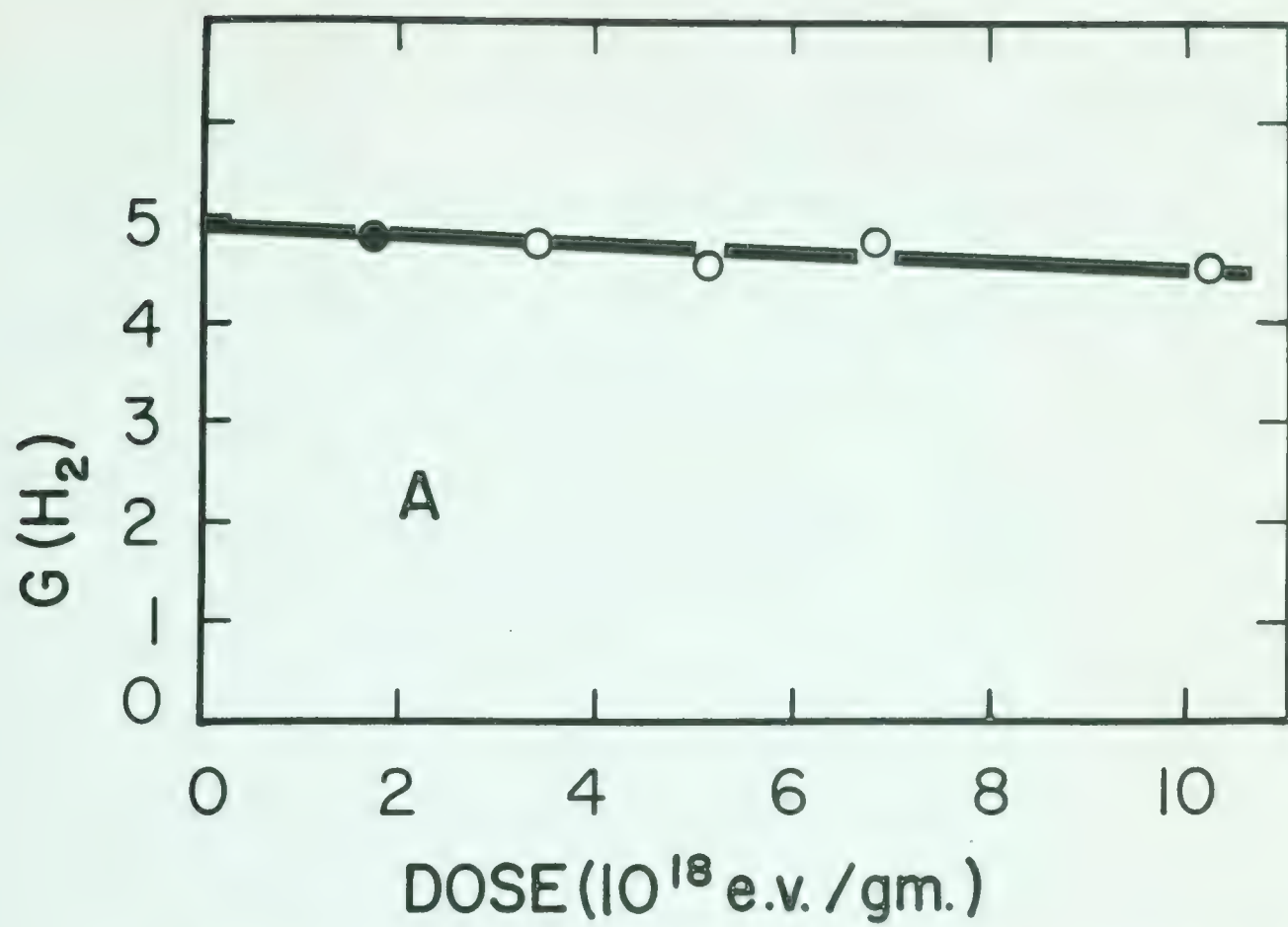






TABLE III-3

HYDROGEN YIELD AS A FUNCTION OF DOSE.  
(Liquid Ethanol Radiolysis)

Dose e.v./gm.	G(H <sub>2</sub> )	Remarks	
		Approximate Dose Rate (e.v./gm.-hr.)	Water Content of Substrate
1) 0.645 x 10 <sup>20</sup>	4.28	0.9 x 10 <sup>18</sup>	0.2%
2) 1.52 x 10 <sup>20</sup>	4.40	0.9 x 10 <sup>18</sup>	0.2%
3) 3.85 x 10 <sup>20</sup>	4.29	0.9 x 10 <sup>18</sup>	0.2%
4) 4.50 x 10 <sup>20</sup>	4.19	0.9 x 10 <sup>18</sup>	0.2%
5) 0.86 x 10 <sup>20</sup>	4.54	0.9 x 10 <sup>18</sup>	0.005%
6) 1.38 x 10 <sup>20</sup>	4.22	0.9 x 10 <sup>18</sup>	0.005%
7) 2.20 x 10 <sup>20</sup>	4.00	0.9 x 10 <sup>18</sup>	0.005%
8) 2.88 x 10 <sup>20</sup>	4.10	0.9 x 10 <sup>18</sup>	0.005%
9) 3.50 x 10 <sup>20</sup>	4.08	0.9 x 10 <sup>18</sup>	0.005%
10) 1.49 x 10 <sup>20</sup>	4.36	5 x 10 <sup>18</sup>	0.005%
11) 3.49 x 10 <sup>20</sup>	4.08	5 x 10 <sup>18</sup>	0.005%
12) 3.50 x 10 <sup>20</sup>	4.20*	6 x 10 <sup>19</sup>	0.005%
13) 3.52 x 10 <sup>20</sup>	4.27*	6 x 10 <sup>19</sup>	0.005%
14) 1.70 x 10 <sup>18</sup>	4.88	5 x 10 <sup>18</sup>	0.005%
15) 1.70 x 10 <sup>18</sup>	4.76	5 x 10 <sup>18</sup>	0.005%
16) 1.71 x 10 <sup>18</sup>	4.92	5 x 10 <sup>18</sup>	0.005%
17) 3.40 x 10 <sup>18</sup>	4.79	5 x 10 <sup>18</sup>	0.005%
18) 5.10 x 10 <sup>18</sup>	4.59	5 x 10 <sup>18</sup>	0.005%
19) 6.79 x 10 <sup>18</sup>	4.85	5 x 10 <sup>18</sup>	0.005%
20) 10.2 x 10 <sup>18</sup>	4.58	5 x 10 <sup>18</sup>	0.005%

\* Analysis by Mass Spectrometry.



values as those employed by ordinary sized gas analysis samples (2 ml.) could not be used. Dosimetry values for the 10 ml. samples were determined and found to be about 30% lower than those for the smaller samples.

The value of  $G(H_2)$  extrapolated to zero dose ( $G_i(H_2)$ ) determined from Figure III-3 is  $4.9 \pm 0.1$ .

### Methane

Values of  $G(CH_4)$  as a function of dose are given in Table III-4 and displayed in Figure III-4(A).

Methane comprised approximately 10% of the  $-196^\circ$  fraction and the scatter in Figure III-4(A) is considerable. Within the limits of precision the plot shows no dependence on total dose. Thus,  $G_i(CH_4)$  0.6 was obtained by averaging the values found. Rather large error limits are attached to this number.

### Carbon Monoxide

This gas constituted approximately 1% of the  $-196^\circ$  gas fraction. Dose versus yield values are given in Table III-5 and are shown in Figure III-4(B). Again, scatter is considerable but there appears to be no dose dependence of  $G(CO)$ .  $G_i(CO)$  was found to be 0.06.

#### ii) Gas Fraction volatile at $-112^\circ C$ .

The gases measured regularly in this fraction were ethane, ethylene and propane. Small amounts of methane were sometimes found in this fraction. When this occurred, this small yield was added to that measured in the  $-196^\circ$  fraction. This amounted to only 1-5% of the total

## FIGURE III-4

VARIOUS GASEOUS PRODUCT YIELDS AS A FUNCTION OF DOSE.  
(Liquid Ethanol Radiolysis)

A. Methane

B. Carbon Monoxide

C. Ethane

● Average of 4 values at 3 different dose rates  
(0.9, 5 and  $60 \times 10^{18}$  e.v./gm.-hr.)  
See Table III-6

D. Ethylene

○ Dose Rate  $\approx 0.9 \times 10^{18}$  e.v./gm.-hr.

◇ Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.

□ Dose Rate  $\approx 6 \times 10^{19}$  e.v./gm.-hr.

(Average of two values)  
See Table III-6

E. Propane

● Average of two values at a dose rate of  
 $6 \times 10^{19}$  e.v./gm.-hr.



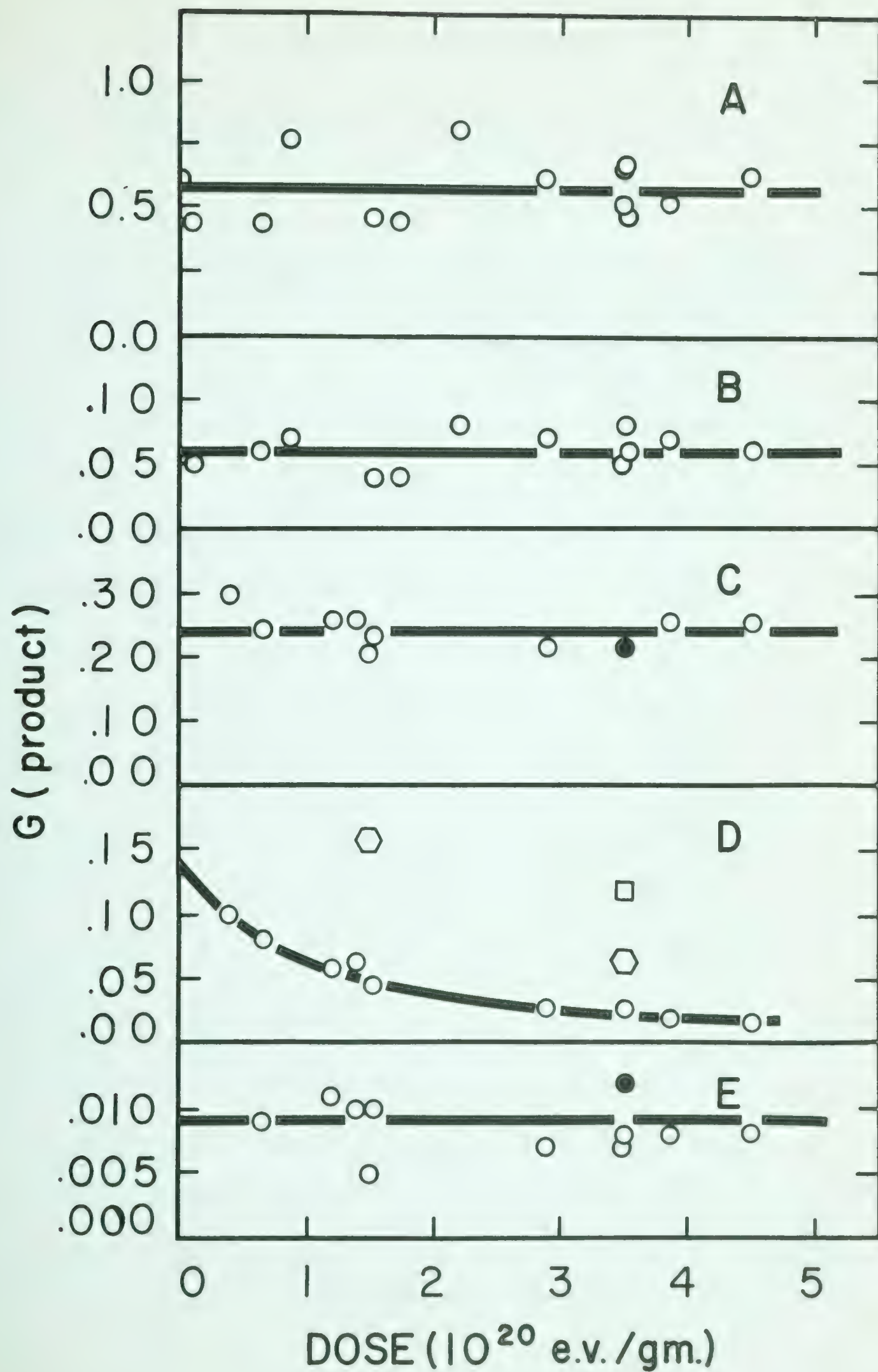






TABLE III-4

## METHANE YIELD AS A FUNCTION OF DOSE

(Liquid Ethanol Radiolysis)

Dose (e.v./gm.)	G(CH <sub>4</sub> )	Remarks	
		Approximate Dose Rate (e.v./gm.-hr.)	Water Content of Substrate
1) 0.645 x 10 <sup>20</sup>	0.43	0.9 x 10 <sup>18</sup>	0.2%
2) 1.52 x 10 <sup>20</sup>	0.46	0.9 x 10 <sup>18</sup>	0.2%
3) 3.85 x 10 <sup>20</sup>	0.51	0.9 x 10 <sup>18</sup>	0.2%
4) 4.50 x 10 <sup>20</sup>	0.61	0.9 x 10 <sup>18</sup>	0.2%
5) 0.865 x 10 <sup>20</sup>	0.77	0.9 x 10 <sup>18</sup>	0.005%
6) 2.20 x 10 <sup>20</sup>	0.80	0.9 x 10 <sup>18</sup>	0.005%
7) 2.88 x 10 <sup>20</sup>	0.61	0.9 x 10 <sup>18</sup>	0.005%
8) 3.50 x 10 <sup>20</sup>	0.67	0.9 x 10 <sup>18</sup>	0.005%
9) 1.70 x 10 <sup>18</sup>	0.62	5 x 10 <sup>18</sup>	0.005%
10) 10.2 x 10 <sup>18</sup>	0.44	5 x 10 <sup>18</sup>	0.005%
11) 1.71 x 10 <sup>20</sup>	0.44	5 x 10 <sup>18</sup>	0.005%
12) 3.49 x 10 <sup>20</sup>	0.65	5 x 10 <sup>18</sup>	0.005%
13) 3.50 x 10 <sup>20</sup>	0.52*	6 x 10 <sup>19</sup>	0.005%
14) 3.52 x 10 <sup>20</sup>	0.46*	6 x 10 <sup>19</sup>	0.005%

\* Analysis by Mass Spectrometry.



TABLE III-5

CARBON MONOXIDE YIELD AS A FUNCTION OF DOSE

( Liquid Ethanol Radiolysis )

Dose (e. v. /gm.)	G(CO)	Remarks	
		Approximate Dose Rate (e. v. /gm. -hr.)	Water Content of Substrate
1) $0.645 \times 10^{20}$	0.06	$0.9 \times 10^{18}$	0.2%
2) $1.52 \times 10^{20}$	0.04	$0.9 \times 10^{18}$	0.2%
3) $3.85 \times 10^{20}$	0.07	$0.9 \times 10^{18}$	0.2%
4) $4.50 \times 10^{20}$	0.06	$0.9 \times 10^{18}$	0.2%
5) $0.865 \times 10^{20}$	0.07	$0.9 \times 10^{18}$	0.005%
6) $2.20 \times 10^{20}$	0.08	$0.9 \times 10^{18}$	0.005%
7) $2.88 \times 10^{20}$	0.07	$0.9 \times 10^{18}$	0.005%
8) $3.50 \times 10^{20}$	0.08	$0.9 \times 10^{18}$	0.005%
9) $10.2 \times 10^{18}$	0.05	$5 \times 10^{18}$	0.005%
10) $1.71 \times 10^{20}$	0.04	$5 \times 10^{18}$	0.005%
11) $3.49 \times 10^{20}$	0.05	$6 \times 10^{19}$	0.005%
12) $3.52 \times 10^{20*}$	0.06	$6 \times 10^{19}$	0.005%

\* Analysis by Mass Spectrometry





TABLE III-6

ETHANE, ETHYLENE AND PROPANE YIELD AS A FUNCTION OF DOSE.

(Liquid Ethanol Radiolysis)

Dose in e.v./gm. of Ethanol	G $C_2H_6$	G $C_2H_4$	G $C_3H_8$	Approximate Dose Rate (e.v./gm. -hr.)	Water Content of Substrate
1) $0.38 \times 10^{20}$	0.299	0.100	-----	$0.9 \times 10^{18}$	0.2%
2) $0.65 \times 10^{20}$	0.243	0.080	0.009	$0.9 \times 10^{18}$	0.2%
3) $1.20 \times 10^{20}$	0.257	0.059	0.011	$0.9 \times 10^{18}$	0.2%
4) $1.52 \times 10^{20}$	0.231	0.046	0.010	$0.9 \times 10^{18}$	0.2%
5) $3.85 \times 10^{20}$	0.252	0.020	0.008	$0.9 \times 10^{18}$	0.2%
6) $4.50 \times 10^{20}$	0.251	0.018	0.008	$0.9 \times 10^{18}$	0.2%
7) $1.38 \times 10^{20}$	0.259	0.064	0.010	$0.9 \times 10^{18}$	0.005%
8) $2.88 \times 10^{20}$	0.214	0.029	0.007	$0.9 \times 10^{18}$	0.005%
9) $3.50 \times 10^{20}$	0.226	0.028	0.008	$0.9 \times 10^{18}$	0.005%
10) $1.49 \times 10^{20}$	0.201	0.159	0.005	$5 \times 10^{18}$	0.005%
11) $3.49 \times 10^{20}$	0.222	0.065	0.007	$5 \times 10^{18}$	0.005%
12) $3.50 \times 10^{20}$	0.220	0.105	0.011	$6 \times 10^{19}$	0.005%
13) $3.52 \times 10^{20}$	0.190	0.137	0.013	$6 \times 10^{19}$	0.005%

Sample 12,  $G(C_2H_2) = 0.016$ Sample 13,  $G(C_2H_2) = 0.0002$  $G(C_2H_2) < 0.02$



methane measured.

Analysis of light ethanol control runs for the deuterated samples was done by mass spectrometry rather than gas chromatography.

Calibration curves for methane, ethane, ethylene and propane were run on the silica gel column used to analyse this gas fraction. All were of the type found for methane and carbon monoxide on charcoal (i.e. a linear dependence of peak area on pressure and zero intercept).

Blank runs for the  $-112^{\circ}$  fraction showed that unless the slush baths were frequently "touched up" by adding liquid nitrogen to them, some ethanol escaped through the traps to the McLeod gauge. Mass spectral analysis showed that careful attention to the state of the slush resulted in an ethanol content of less than 1% in the  $-112^{\circ}$  fraction at a dose of  $3.50 \times 10^{20}$  e.v./gm.

### Ethane

Ethane yields at various doses are listed in Table III-6 and the plot of these values is given in Figure III-4(C). This graph shows no evidence of dose dependence over the range studied.  $G_i(\text{ethane}) = 0.24$ .

### Ethylene

$G(\text{ethylene})$  as a function of dose is given in Figure III-4(D). The values used for the plot are given in Table III-6. Yields obtained at a dose rate of approximately  $0.9 \times 10^{18}$  e.v./gm.-hr. fitted a curve which extrapolated to a  $G_i(\text{ethylene}) = 0.14$ . This plot showed a definite dose dependence. The yield of ethylene decreased with dose rather sharply



at first and then continued to decrease more slowly.

Two samples irradiated at a dose rate of  $5 \times 10^{18}$  e.v./gm.-hr. showed significantly higher values than those used for the above mentioned curve. An average value given by two samples radiolysed at a dose rate of  $6 \times 10^{19}$  e.v./gm.-hr. to  $3.5 \times 10^{20}$  e.v./gm.- showed a higher ethylene value than samples at lower dose rates but having the same absorbed dose.

### Propane

Figure III-4(E) and Table III-6, which present  $G(\text{propane})$  and total dose values, indicate no dependence of propane yield upon dose.

$$G_i(\text{propane}) = 0.009.$$

### Acetylene

Mass spectrometry revealed the presence of acetylene in the -112° fraction. From the values obtained it could be established that  $G(\text{acetylene}) < 0.02$ .

Synthetic samples showed that the sensitivity of acetylene to the gas chromatographic apparatus was low, due to its broad peak, and therefore it escaped detection by this method of analysis.

### Butane

In a sample that received a total dose of  $2.5 \times 10^{21}$  e.v./gm. a further small gas chromatographic peak was obtained. Peak shape and retention time on the silica gel column indicated that this peak was butane. The  $G$  value for this product was approximately  $5 \times 10^{-4}$ .





b) Liquid Productsi) Acetaldehyde

Acetaldehyde was a major product of the radiolysis. Initial attempts at acetaldehyde determination were by gas chromatography using a 2.5 meter Carbowax 1500 on Fluoropak column. The method was unsatisfactory.

Polarography, in conjunction with acetal analysis on a 2.5 meter di-n-decyl phthalate column was later used to determine  $G(\text{acetaldehyde})$ . The yield of acetal (each molecule of which is equivalent to one molecule of aldehyde) was combined with acetaldehyde, determined polarographically, to give  $G_{\text{total}}(\text{acetaldehyde})$ .

The variation of the G value of acetaldehyde (total) with dose is shown in Figure III-5(A) and the values are tabulated in Table III-7. The yield appears to be independent of dose and dose rate.  $G_i(\text{acetaldehyde}) = 1.9$ .

ii) Formaldehyde

The G values for this product are given in Figure III-5(B) and Table III-7. The scatter of the values is considerable but no dependence upon dose is evident.  $G_i(\text{formaldehyde}) = 0.13$ . Attached to this number, however, is a large degree of uncertainty due to experimental error.

iii) Glycols

All glycol yields reported were obtained using a 2.5 meter di-n-decyl phthalate column. The glycols were separated on this column in the following order; ethylene glycol, 1,2-propanediol, 2,3-butanediol,

## FIGURE III-5

VARIOUS LIQUID PRODUCT YIELDS AS A FUNCTION OF DOSE.

(Liquid Ethanol Radiolysis)

A.  $\text{CH}_3\text{CHO}$ 

● Average of two values (see Table III-7)

● Average of three values (see Table III-7)

B.  $\text{HCHO}$ 

C. 2,3-Butanediol

● Average of two values (see Table III-8)

● Average of four values (see Table III-8)

D. 1,2-Propanediol

● Average of four values (see Table III-8)

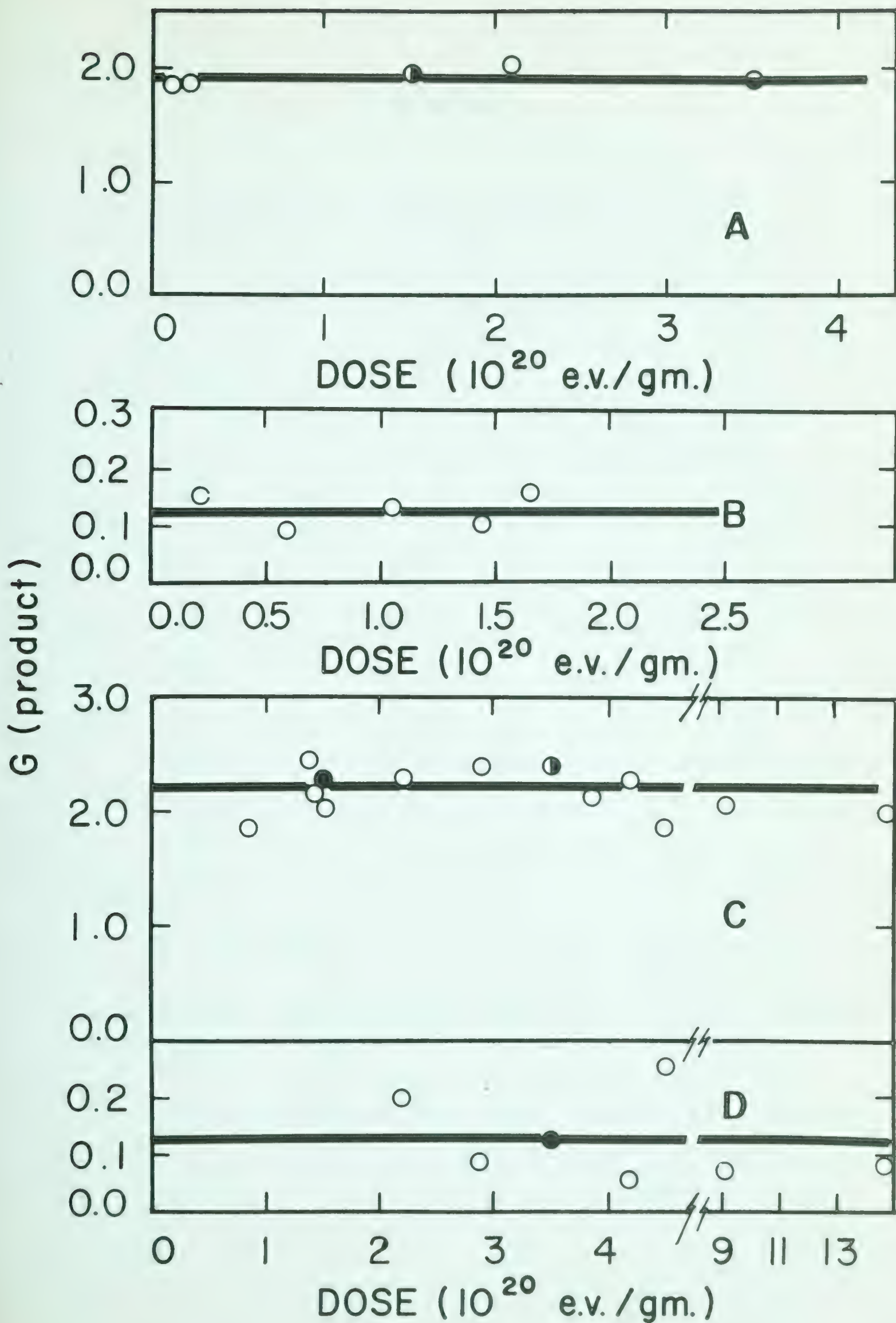






TABLE III-7

ALDEHYDE YIELD AS A FUNCTION OF DOSE.

(Liquid Ethanol Radiolysis)

Dose (e.v./gm.)	G(CH <sub>3</sub> CHO)	Dose (e.v./gm.)	G(HCHO)
0.11 x 10 <sup>20</sup>	1.85	0.22 x 10 <sup>20</sup>	0.15
0.22 x 10 <sup>20</sup>	1.87	0.58 x 10 <sup>20</sup>	0.09
1.49 x 10 <sup>20</sup>	1.88	1.05 x 10 <sup>20</sup>	0.13
1.50 x 10 <sup>20</sup>	2.02	1.44 x 10 <sup>20</sup>	0.10
2.10 x 10 <sup>20</sup>	2.04	1.65 x 10 <sup>20</sup>	0.16
3.50 x 10 <sup>20</sup>	1.88		
3.50 x 10 <sup>20</sup> *	1.84		
3.52 x 10 <sup>20</sup> *	1.81		

\* Dose rate for these two samples 6 x 10<sup>19</sup> e.v./gm.-hr.

Dose rate for all other samples 5 x 10<sup>18</sup> e.v./gm.-hr.



TABLE III-8  
GLYCOL YIELD AS A FUNCTION OF DOSE.

(Liquid Ethanol Radiolysis)

Dose in e.v./gm.	G(2,3-Butane- diol)	G(1,2-Propane- diol)	Remarks	
			Water Content	Dose Rate in e.v./gm.-hr.
1) $1.52 \times 10^{20}$	2.04		0.2%	$0.9 \times 10^{18}$
2) $3.85 \times 10^{20}$	2.14		0.2%	$0.9 \times 10^{18}$
3) $4.50 \times 10^{20}$	1.86	0.25	0.2%	$0.9 \times 10^{18}$
4) $0.86 \times 10^{20}$	1.85		0.005%	$0.9 \times 10^{18}$
5) $1.38 \times 10^{20}$	2.46		0.005%	$0.9 \times 10^{18}$
6) $2.20 \times 10^{20}$	2.30	0.20	0.005%	$0.9 \times 10^{18}$
7) $2.88 \times 10^{20}$	2.41	0.09	0.005%	$0.9 \times 10^{18}$
8) $3.50 \times 10^{20}$	2.41	0.15	0.005%	$0.9 \times 10^{18}$
9) $1.44 \times 10^{20}$	2.16		0.005%	$5 \times 10^{18}$
10) $1.49 \times 10^{20}$	2.24		0.005%	$5 \times 10^{18}$
11) $1.50 \times 10^{20}$	2.30		0.005%	$5 \times 10^{18}$
12) $3.49 \times 10^{20}$	2.34	0.11	0.005%	$5 \times 10^{18}$
13) $4.18 \times 10^{20}$	2.27	0.06	0.005%	$5 \times 10^{18}$
14) $3.50 \times 10^{20}$	2.32	0.12	0.005%	$6 \times 10^{19}$
15) $3.52 \times 10^{20}$	2.54	0.12	0.005%	$6 \times 10^{19}$
16) $9.19 \times 10^{20}$	2.06	0.07	0.005%	$5 \times 10^{18}$
17) $14.54 \times 10^{20}$	2.00	0.08	0.005%	$5 \times 10^{18}$

Samples 8, 12, 14, and 15 were averaged for Figure III-5 Section C.

Samples 10 and 11 were averaged for Figure III-5 Section C.



1,3-propanediol, 1,3-butanediol, 1,4-butanediol.

### 2,3-Butanediol

This glycol had the largest G value of any liquid product.

Table III-8 and Figure III-5(C) contain G(2,3-butanediol) and total dose values. The yield seems to be essentially constant with dose.

$$G_1(2,3\text{-butanediol}) = 2.2.$$

At high doses ( $\approx 9 \times 10^{20}$  e.v./gm.) the 2,3-butanediol was resolved into two distinct peaks on the di-n-decyl phthalate column. With the aid of a sample of d,l-2,3-butanediol from Prof. F.A.L. Anet<sup>(99)</sup> it was established that the two peaks were due to d,l and meso-2,3-butane-diol.

### 1,2-Propanediol

At doses greater than  $2 \times 10^{20}$  e.v./gm. 1,2-propanediol could be detected in irradiated samples. The small peak sizes resulted in rather scattered results. Attempts to get larger 1,2-propanediol peaks by prolonged irradiation resulted in poorer separation due to broadening of the 2,3-butanediol peak. Figure III-5(D) and Table III-8 contain the data collected for 1,2-propanediol.  $G_1(1,2\text{-propanediol}) = 0.13$ .

### Other Glycols

A very high dose sample ( $3 \times 10^{21}$  e.v./gm.) was used to detect any other glycols that may arise from ethanol radiolysis. When this sample was gas chromatographed, measurable 1,2-propanediol, 2,3-butanediol, ethylene glycol and 1,3-butanediol peaks were obtained. Indications of very small amounts of other products were evident. Slow





TABLE III-9

RELATIVE AMOUNTS OF GLYCOLS FROM THE RADIOLYSIS OF LIQUID  
ETHANOL

Glycol	Amount in Arbitrary Units	G(Diol)*
Ethylene glycol	1.0	0.01
1,2-Propanediol	27.0	0.27
1,3-Propanediol	0.22	0.002
2,3-Butanediol	221	2.24
1,3-Butanediol	4.6	0.047
1,4-Butanediol	1.14	0.012

\* Based on assumed  $G(2,3\text{-butanediol}) = 2.24$ .

Dose =  $30 \times 10^{20}$  e.v./gm.



evaporation of the alcohol to about one quarter its original volume to concentrate these compounds, and subsequent injection onto the di-n-decyl phthalate column resulted in measurable peaks for 1,4-butanediol and 1,3-propanediol. As the boiling points of the glycols range from 185-230°C, it is reasonable to assume that negligible amounts of these compounds were lost during the evaporation of the ethanol (boiling point = 78°C). Ethylene glycol could be detected without evaporating any sample, while 1,4-butanediol could not, even though both were present in approximately the same amounts. This was due to the fact that the C<sub>2</sub> glycol peak was sharp while 1,4-butanediol exhibited a very broad peak.

The relative amounts of the six glycols measured are contained in Table III-9.

iv) Sec.-Butyl Alcohol.

At doses greater than  $4 \times 10^{20}$  e.v./gm. a peak occurring rather high on the ethanol tail, using the di-n-decyl phthalate column, was observed. Sec-butyl alcohol gave an identical retention time when injected under identical conditions. When a small amount of sec.-butyl alcohol was added to a sample in which this peak was visible, it grew with no apparent change in peak shape. Based upon this evidence the peak was considered to be due to sec.-butyl alcohol.

This peak was measured in three samples that received  $\approx 4, 9,$  and  $14.5 \times 10^{20}$  e.v./gm.. Calibration using sec.-butyl alcohol indicated that these samples had G(sec.-butyl alcohol) values of 0.012, 0.072 and





0.080 respectively. As the value of 0.012 was determined on a very small peak and the base line position high on the ethanol tail was uncertain, this value was deemed untrustworthy. For this reason  $G(\text{sec. -butyl alcohol})$  is considered to be  $\approx 0.08$ .

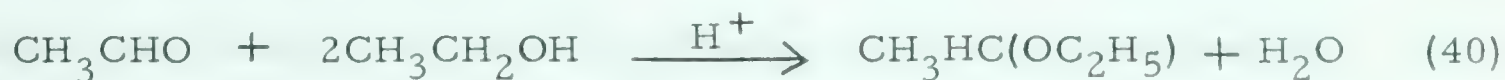
v) Unidentified Peak.

A peak of approximately the same size as that assigned the identity of sec. -butyl alcohol was present between acetal and ethylene glycol on the di-n-decyl phthalate column chromatogram at doses above  $4 \times 10^{20}$  e.v./gm.. All attempts to identify this product were unsuccessful. Assuming the same calibration factor as that for sec. -butyl alcohol this product would have a  $G$  value of  $\approx 0.05$ .

vi) Water.

1) Role of Acetal in Water Analysis.

Initial values for  $G(\text{water})$  were very scattered and considered untrustworthy. Later 1,1-diethoxyethane (acetal) was identified as a secondary product of the radiolysis. The overall reaction for its formation is as below.



Thus, for each molecule of acetal formed, one molecule of water is generated. Hence  $G_{\text{true}}(\text{H}_2\text{O}) = G_{\text{observed}}(\text{H}_2\text{O}) - G(\text{acetal})$ .

Details for the simultaneous analysis of water and acetal have been given in the Experimental Section.

Identification of acetal as a product was accomplished by



comparison of retention time for the peak in the irradiated sample with ethanol solutions containing British Drug House acetal. Acetal was added to an irradiated sample containing the peak suspected to be acetal and the peak grew on di-n-decyl phthalate and Carbowax 1500 columns with no change in peak shape. "Neat" injections of acetal were also run to prove the increase in peak area was due to acetal itself and not an impurity in the acetal.

This gas chromatographic identification was supplemented by mass spectral analysis. The peak from the irradiated alcohol was trapped after separation on the di-n-decyl phthalate column and a cracking pattern of the trapped material was obtained from a mass spectrometer (76 e.v. electron bombardment). Next, the peak from a synthetic solution of ethanol and acetal was treated similarly. Finally, a solution of acetaldehyde and ethanol was very slightly acidified with sulphuric acid and gas chromatographed at various intervals. A peak with the same retention time as acetal grew and was subsequently trapped and subjected to mass spectral analysis. The cracking patterns of these three trapped peaks are compared in Table III-10. No  $m/e$  values less than 73 are reported as it was later found that the British Drug House acetal sample contained considerable methyl ethyl ketone. This compound appeared on the chromatogram close to the acetal peak. There was sufficient separation to preclude methyl ethyl ketone's presence in measurable quantities in the irradiated sample but not enough to exclude its presence in the trapped off peak in the synthetic mixture of ethanol and acetal. The molecular





TABLE III-10

## MASS SPECTRAL ANALYSIS FOR ACETAL.

m/e	76 e.v. bombardment			20 e.v. bombardment	
	a	b	c	a	b
73	100.0	100.0	100.0	100.0	100.0
74	3.9	9.7	2.8		
75	2.4	5.3	$\approx 1$		
85	3.1	2.7	6.3		
86	5.5	4.5	4.3		
87	24.2	21.9	20.6	28.6	22.9
88	3.9	2.7	$\approx 1$		
89	14.0	13.0	14.3	14.3	13.7
100	18.0	18.0	17.5	14.3	18.3
101	68.6	70.0	71.5	82.1	87.0
102	3.1	3.6	$\approx 1$		
103	6.7	3.6	7.2		
116	8.6	5.3	5.6		
117	38.3	35.3	29.7	71.5	52.5
118	3.9	3.1	$\approx 1$		

- a) Trapped gas chromatographic peak from irradiated sample considered to be acetal.
- b) Trapped gas chromatographic peak of acetal in ethanol (British Drug House Co. Acetal).
- c) Trapped gas chromatographic peak from a slightly acidic solution of acetaldehyde in ethanol.





weight of methyl ethyl ketone = 72.

The reasonable agreement of the mass spectral cracking patterns, combined with the retention time coincidence on the two gas chromatographic columns served to establish positive identification of the radiolysis product as acetal.

## 2) Dosimetry for Water Analysis Samples.

It was considered impractical to carry out dosimetry at a volume of 0.1 ml. (the volume of the samples employed) as  $\approx 1$  ml. of  $\text{Fricke}$  solution is needed for analysis. Hence, dosimetry data previously collected for various other sample sizes were plotted and the resulting line was extrapolated to a volume of 0.1 ml.. This plot is given in Figure III-6 and the numbers used are displayed in Table III-11. These measurements were determined for one sample position. Proportionate corrections to 0.1 ml. dosimetry were applied to three other positions, the dosimetry of which was known for larger volumes. As the dose rates for all four positions at 2.2 ml. dosimetry were the same within 20%, this type of correction should introduce no serious error in dosimetry ( $< 2\%$ ).

## 3) G(Water).

Due to the expected low true G value for water and its rather broad peak on Carbowax 1500, the samples to be analysed were given relatively large doses. The dose range employed was  $5.8 - 56.4 \times 10^{20}$  e.v./gm..

Plots of G(water and G(acetal) versus absorbed dose are given

FIGURE III-6

DEPENDENCE OF DOSE RATE UPON SAMPLE VOLUME.

(Cobalt "Bomb" Irradiations)

Dose rates were measured at different dates but were all "normalized" to the same date (June 8, 1961).

Measurements were made for 1 sample position.

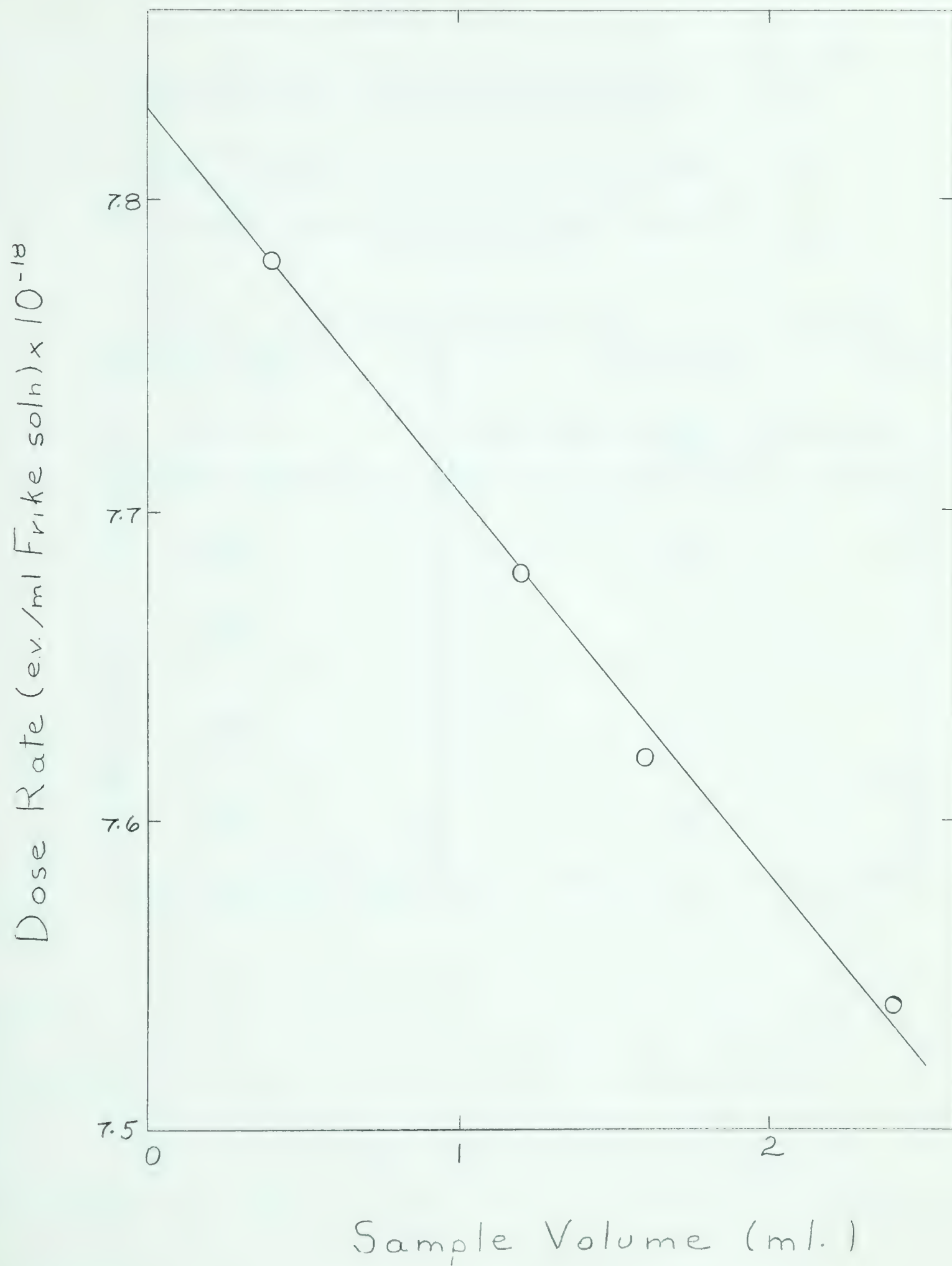






TABLE III-11

DOSE RATE AS A FUNCTION OF SAMPLE  
VOLUME FOR COBALT "BOMB" IRRADIATIONS.

(for Sample Positions Used for Water Analysis).

Sample Volume (ml.)	Dose Rate (e.v./ml. of Fricke Solution-hr) $\times 10^{-18}$
0.40	7.78
1.20	7.68
1.60	7.62
2.20	7.54



in Figure III-7. The values used for this graph are presented in Table III-12. Despite the subtraction of a relatively large  $G(\text{Acetal})$ , Figure III-7 shows low scatter for  $G(\text{H}_2\text{O})$ , and shows no dependence of  $G(\text{water})$  with dose over the range studied.  $G(\text{water}) = 0.5$ .

It will be noted that  $G(\text{acetal})$  is very scattered and higher than  $G(\text{acetaldehyde})$  shown in Figure III-5. The scatter of the points is not surprising, as it was observed that in samples involving acetaldehyde and acetal analysis, the relative proportions of the two, varied widely from sample set to sample set and even between samples in the same set. Consequently the low values of acetal shown in Figure III-7 are probably due to aldehyde not converted to acetal.

To check the value of acetal from these samples, alcohol used for water analysis was radiolysed to  $1.5 \times 10^{20}$  e.v./gm.. This sample was then analysed for hydrogen, acetaldehyde, acetal and 2,3-butanediol. The following results were obtained:  $G(\text{hydrogen}) = 5.1$ ,  $G(\text{acetal}) = 3.6$ ,  $G(\text{acetaldehyde}) = 0.0$ ,  $G(2,3\text{-butanediol}) = 1.5$ .

$G(\text{hydrogen})$  and  $G(\text{acetal} + \text{acetaldehyde})$  are both higher than usually observed. Fletcher<sup>(45)</sup> has shown that slightly acidic liquid ethanol (0.001M  $\text{H}_2\text{SO}_4$ ) yields a  $G(\text{hydrogen})$  of  $\approx 5.2$  with  $G(\text{acetal}) \approx 3.4$ .

It thus appears, that the high yield of acetal exhibited by the water analysis samples is due to a small amount of acid present.

### c) Summary.

The yields of all products identified and measured from the

FIGURE III-7

WATER AND ACETAL YIELDS AS A FUNCTION OF  
DOSE .

(Liquid Ethanol Radiolysis)

□ G(acetal plus water)

● G(acetal)

○ G(water)

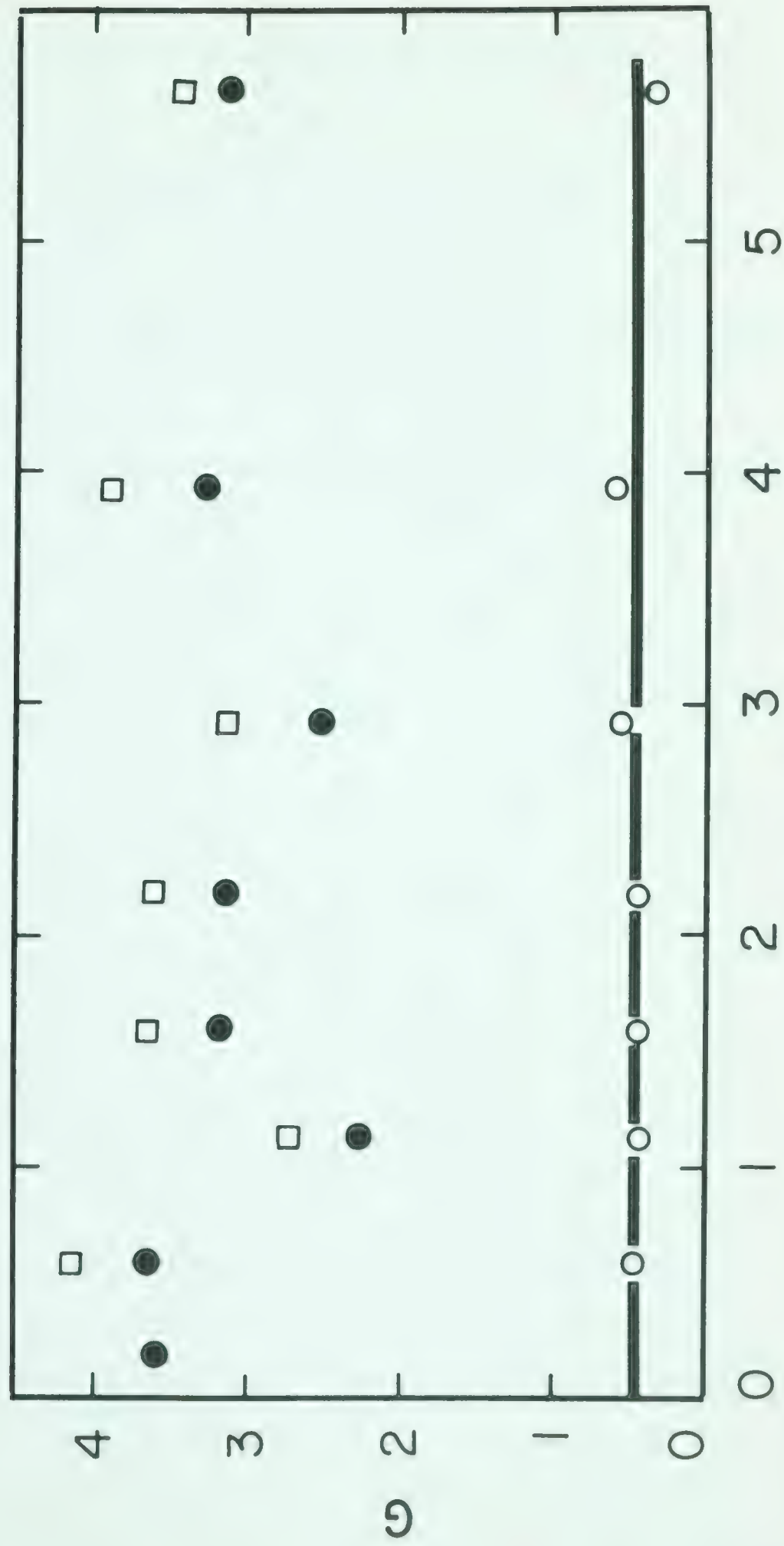






TABLE III-12

WATER AND ACETAL YIELDS AS A FUNCTION OF  
DOSE.

(Liquid Ethanol Radiolysis)

Total Dose (e.v./gm.)	G(Water )	G(Acetal)	G(Acetal + Water)
$5.8 \times 10^{20}$	0.49	3.65	4.14
$11.3 \times 10^{20}$	0.45	2.28	2.73
$15.8 \times 10^{20}$	0.46	3.19	3.65
$21.7 \times 10^{20}$	0.46	3.15	3.61
$29.1 \times 10^{20}$	0.59	2.52	3.11
$39.2 \times 10^{20}$	0.60	3.28	3.88
$56.4 \times 10^{20}$	0.33	3.11	3.44
$1.90 \times 10^{20}$	--	3.60	--

Dose rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.



radiolysis of liquid ethanol are tabulated in Table III-13. Various dose ranges were used depending upon the analytical method and the G value of the compound in question. For the major products, initial G values were obtained by extrapolating to zero dose ( $G_i$ ). Several of the minor products were measured at one or two specified doses as they were not detectable in the dose range normally employed.

#### B) Ethanol - Benzene Solutions.

A number of binary solutions of ethanol and benzene of varied relative concentrations were radiolyzed to study the possible inhibitory effect of benzene. All these samples were given the same dose ( $1.50 \pm 0.06 \times 10^{20}$  e.v./gm.). The data collected for this type of sample are presented as  $G(\text{product})$  as a function of  $\epsilon_b$ , where  $\epsilon_b$  is the electron fraction of benzene in the sample.

$\epsilon_b$  is defined as:

$$\frac{E_B V_B}{E_B V_B + E_E V_E}$$

where  $E_B$  and  $E_E$  are the electron densities (moles of electrons/ml) of benzene and ethanol respectively, and  $V_B$  and  $V_E$  are their volumes present in the samples.

The products measured in these binary mixtures were hydrogen, methane, ethane, ethylene, acetaldehyde and 2,3-butanediol. Carbon monoxide and propane were also measured but their yields are small and





TABLE III-13

YIELDS OF OBSERVED PRODUCTS FROM THE RADIOLYSIS OF LIQUID  
ETHANOL.

A. GASEOUS PRODUCTS				
Product	G Value	Lowest Dose Used (e.v./gm.)	Dose Rate	Remarks
Hydrogen	4.9	$1.7 \times 10^{18}$	a,b,c	$G_i$
Methane	0.6	$1.7 \times 10^{18}$	a,b,c	$G_i$
Carbon Monoxide	0.06	$1.0 \times 10^{19}$	a,b,c	$G_i$
Ethane	0.24	$4.0 \times 10^{19}$	a,b,c	$G_i$
Ethylene	0.14	$4.0 \times 10^{19}$	a	$G_i$
Propane	0.009	$6.5 \times 10^{19}$	a,b,c	$G_i$
Acetylene	$< 0.02$	$3.5 \times 10^{20}$	c	$G_i^1$
Butane	$5 \times 10^{-4}$	$2.5 \times 10^{20}$	b	$G^1$
B. LIQUID PRODUCTS				
Water	0.5	$5.8 \times 10^{20}$	b	$G_i^2$
Formaldehyde	0.13	$2.2 \times 10^{19}$	b	$G_i$
Acetaldehyde	1.9	$1.1 \times 10^{19}$	b,c	$G_i$
2,3-Butanediol	2.2	$9.0 \times 10^{19}$	a,b,c	$G_i$
1,2-Propanediol	0.13	$2.2 \times 10^{20}$	a,b,c	$G_i$
Ethylene glycol	0.01	$3.0 \times 10^{21}$	b	3
1,3-Propanediol	0.002	$3.0 \times 10^{21}$	b	3
1,3-Butanediol	0.05	$3.0 \times 10^{21}$	b	3
1,4-Butanediol	0.01	$3.0 \times 10^{21}$	b	3
Sec.-Butyl alcohol	0.08	$9.2 \times 10^{20}$	b	4

Dose Rate Column: a) Dose Rate  $\approx 0.9 \times 10^{18}$  e.v./gm.-hr.  
b) Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.  
c) Dose Rate  $\approx 6 \times 10^{19}$  e.v./gm.-hr.

- 1) G value at specified dose.
- 2) Measured in conjunction with acetal yields (see Table III-12) .
- 3) G values obtained from the ratios given in Table III-9 and assuming  $G(2,3\text{-butanediol}) = 2.24$ .
- 4) Average value for two samples of dose  $9.2 \times 10^{20}$  e.v./gm. and  $14.5 \times 10^{20}$  e.v./gm..



at this relatively low dose the results were not reliable especially with samples containing appreciable amounts of benzene. Hence, carbon monoxide and propane data were not plotted.

#### a) Gaseous Products.

##### i) Hydrogen

The yield of hydrogen from these samples as a function of  $\epsilon_b$  is given in Figure III-8(A) and Table III-14. The dashed line in the figure represents the  $G(\text{hydrogen})$  to be expected if the benzene and ethanol were unaffected by the presence of each other during radiolysis; i.e.

$$G(\text{H}_2)_X = G(\text{H}_2)_E^0 \times \epsilon_E + G(\text{H}_2)_B^0 \times \epsilon_B$$

where  $G(\text{H}_2)_X$  is the expected yield,  $G(\text{H}_2)_E^0$  is the hydrogen yield from pure ethanol,  $G(\text{H}_2)_B^0$  is the hydrogen yield from pure benzene and the  $\epsilon$ 's are the respective electron fractions:

Figure III-8(A) shows that benzene inhibits hydrogen formation from liquid ethanol to a considerable extent.

##### ii) Methane

The variation of  $G(\text{methane})$  with  $\epsilon_b$  is given in Figure III-8(B), the data for which are included in Table III-14. The results show considerable scatter, especially at the low benzene concentration section of the plot. Nevertheless, there is evidence of inhibition of this product. The effect of benzene on methane, however, is much less than that on hydrogen. The dashed line refers to  $G(\text{CH}_4)_X$ .

##### iii) Ethylene

The  $G$  value versus  $\epsilon_b$  plot for ethylene is that of Figure III-9(A).

## FIGURE III-8

HYDROGEN AND METHANE YIELDS FROM THE RADIOLYSIS  
OF ETHANOL-BENZENE SOLUTIONS.

$\epsilon_b$  = electron fraction of benzene in the sample.

A: Hydrogen

●  $G_{\text{initial}}(\text{H}_2)$

B: Methane

●  $G_{\text{initial}}(\text{CH}_4)$

Dashed lines represent  $G_X$  (G value expected if there is no interaction between ethanol and benzene).



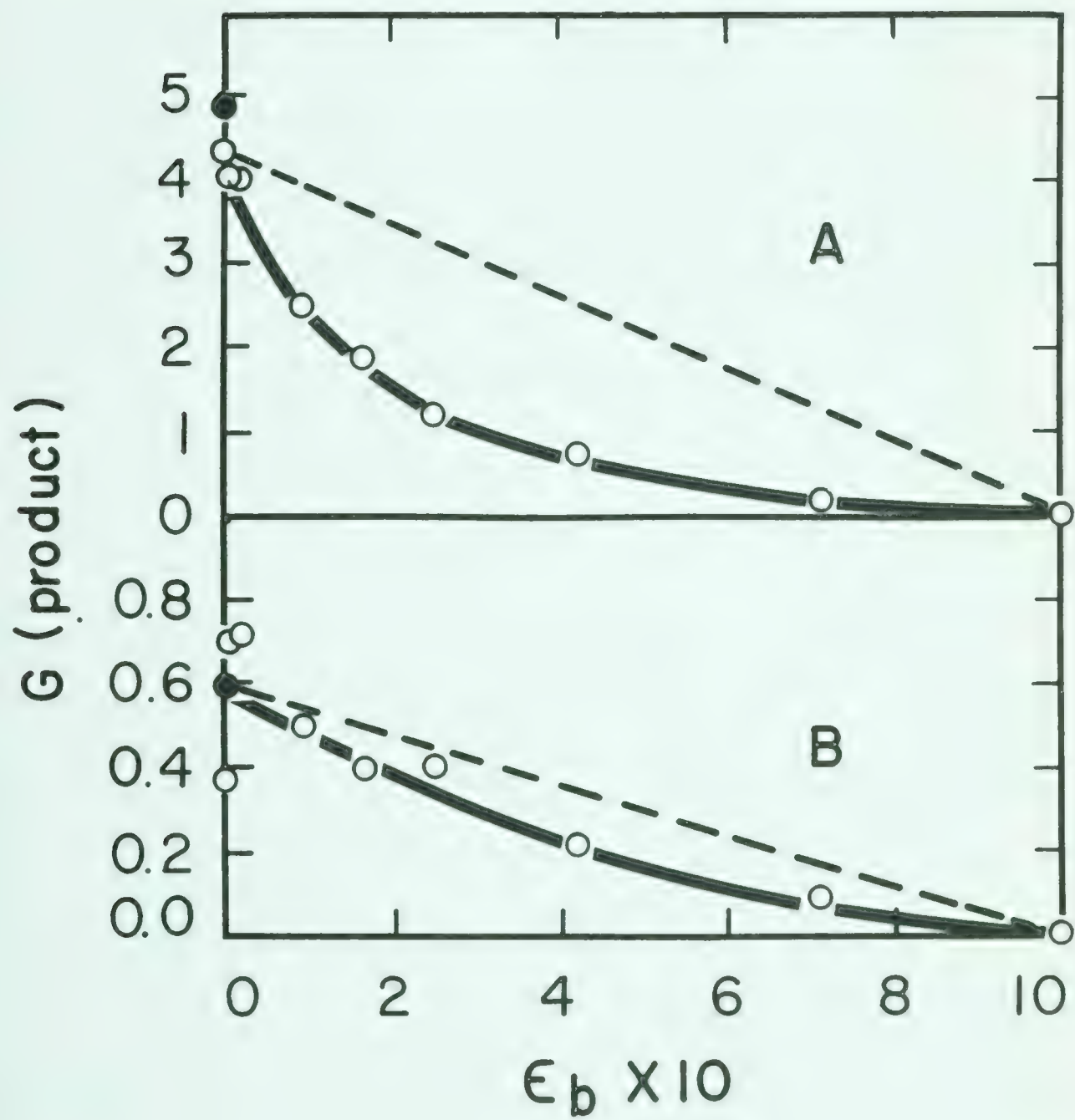






TABLE III-14

-196°C GAS FRACTION PRODUCT YIELDS AS A FUNCTION OF  $\epsilon_b$ .

(Ethanol-Benzene Solution Radiolysis)

All samples received approximately the same dose (see column 2 below).

Approximate Dose Rate =  $5 \times 10^{18}$  e.v./gm.-hr.

$\epsilon_b$	Dose e.v./gm.	G(H <sub>2</sub> )	G(CH <sub>4</sub> )	G(CO)*	G(-196)
1) 0	$1.49 \times 10^{20}$	4.36	0.38	---	4.74
2) $7.35 \times 10^{-3}$	$1.50 \times 10^{20}$	4.06	0.69	0.034	4.77
3) $2.12 \times 10^{-2}$	$1.49 \times 10^{20}$	3.98	0.70	0.040	4.72
4) $9.19 \times 10^{-2}$	$1.48 \times 10^{20}$	2.50	0.50	0.00	3.00
5) 0.165	$1.44 \times 10^{20}$	1.88	0.40	0.051	2.31
6) 0.250	$1.47 \times 10^{20}$	1.20	0.40	0.004	1.61
7) 0.421	$1.50 \times 10^{20}$	0.73	0.22	---	0.94
8) 0.708	$1.51 \times 10^{20}$	0.18	0.08	---	0.26
9) 1.0 00	$1.56 \times 10^{20}$	0.038	0.00	---	0.038

$\epsilon_b$  = electron fraction of benzene in the solution irradiated.

\* Due to the difficulty in obtaining sufficient accuracy in the G(CO) values, no plot of G(CO) versus  $\epsilon_b$  is presented.

## FIGURE III-9

ETHYLENE AND ETHANE YIELDS FROM THE RADIOLYSIS  
OF ETHANOL-BENZENE SOLUTIONS.

$\epsilon_b$  = electron fraction of benzene in the sample.

A: Ethylene

B: Ethane

Dashed lines represent  $G_X$ .

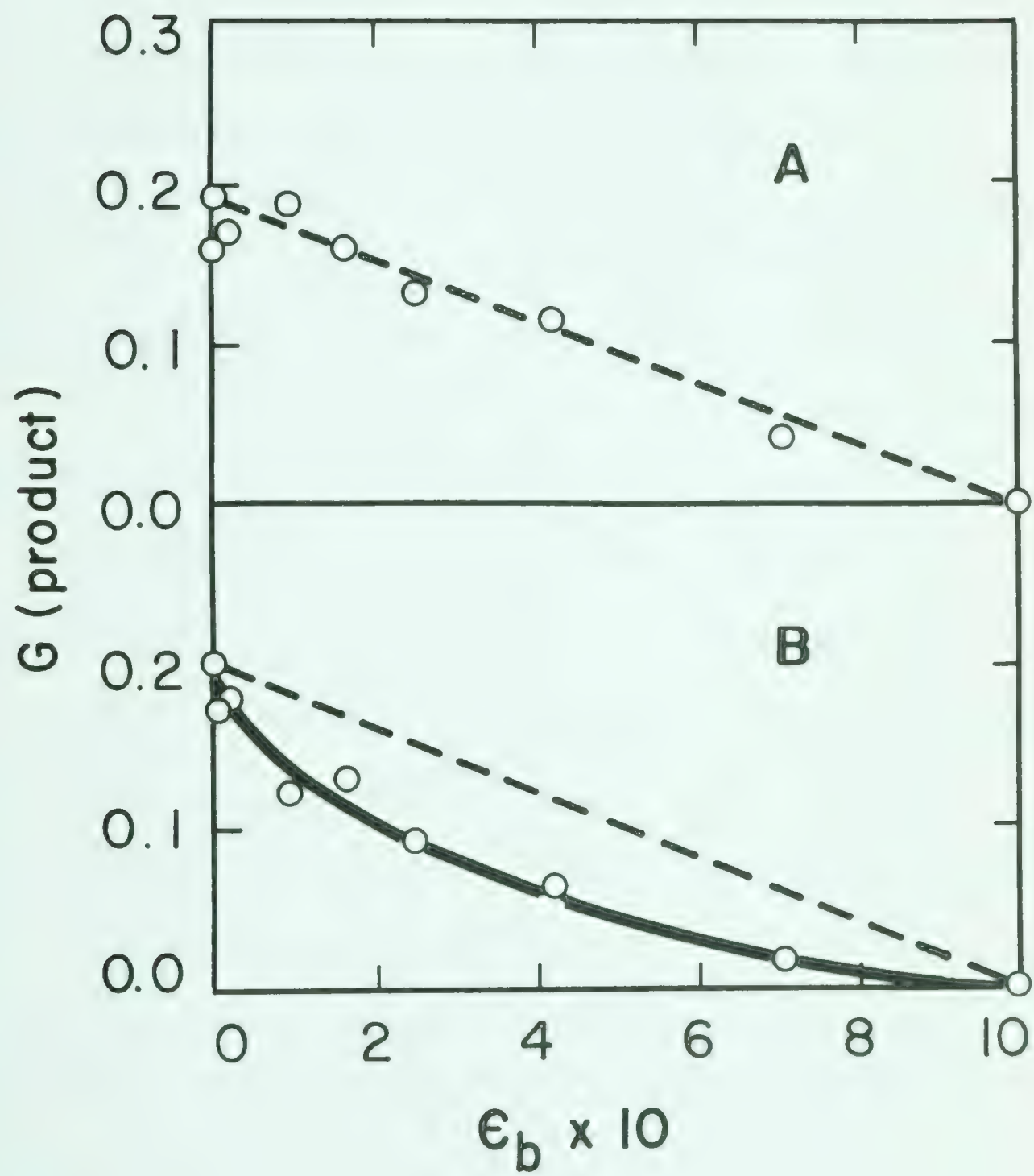






TABLE III-15

-112°C GAS FRACTION PRODUCT YIELDS AS A FUNCTION OF  $\epsilon_b$ .

(Ethanol-Benzene Solution Radiolysis)

All samples received approximately the same dose (see column 2 below).

Approximate Dose Rate =  $5 \times 10^{18}$  e.v./gm.-hr.

$\epsilon_b$	Dose e.v./gm.	G(C <sub>2</sub> H <sub>6</sub> )	G(C <sub>2</sub> H <sub>4</sub> )	G(C <sub>3</sub> H <sub>8</sub> )	G(-112)
1) 0	$1.49 \times 10^{20}$	0.201	0.159	0.005	0.365
2) $7.35 \times 10^{-3}$	$1.50 \times 10^{20}$	0.173	0.193	---	0.366
3) $2.12 \times 10^{-2}$	$1.49 \times 10^{20}$	0.180	0.170	---	0.350
4) $9.19 \times 10^{-2}$	$1.48 \times 10^{20}$	0.121	0.189	---	0.310
5) 0.165	$1.44 \times 10^{20}$	0.130	0.160	0.0035	0.294
6) 0.250	$1.47 \times 10^{20}$	0.091	0.133	---	0.224
7) 0.421	$1.50 \times 10^{20}$	0.064	0.115	0.005	0.184
8) 0.708	$1.51 \times 10^{20}$	0.016	0.041	---	0.057
9) 1.000	$1.56 \times 10^{20}$	---	---	---	0.016*

\* mostly acetylene<sup>(100)</sup>

$\epsilon_b$  = electron fraction of benzene in the solution irradiated.



Table III-15 records the data. The points fall closely on the dashed line, indicating that benzene has little effect upon the production of ethylene from the radiolysis of liquid ethanol.

#### iv) Ethane

Figure III-9(B) and Table III-15, which contain the data for the dependence of  $G(\text{ethane})$  upon  $\epsilon_b$ , show inhibition of formation of this product by benzene.

#### b) Liquid Products.

At the dose employed for the radiolysis of the ethanol-benzene binary mixtures ( $1.50 \times 10^{20}$  e.v./gm.), the only liquid products that could be measured were acetaldehyde and 2,3-butanediol.

#### i) Acetaldehyde

Figure III-10(A) and Table III-16 contain the data relating to the  $\epsilon_b$  dependence of  $G(\text{acetaldehyde})$ . Unfortunately, the values of  $G(\text{acetaldehyde})$ , which should actually be  $G(\text{acetaldehyde} + \text{acetal})$ , at most  $\epsilon_b$  values are only minimum values. This is due to the fact that acetal could not be measured at benzene concentrations  $\epsilon_b > 0.01$  because the benzene peak covered up any acetal peak that might be in the chromatogram. Hence, the values plotted in Figure III-11 for  $\epsilon_b > 0.01$  represent only the aldehyde measured polarographically. Despite this limitation, it is seen that most points fall near the dashed line, which suggests that benzene has little effect upon the formation of acetaldehyde in these solutions.





ii) 2,3-Butanediol

The 2,3-butanediol inhibition curve is given by Figure III-10(B). The values for this plot are given by Table III-17. The glycol yield is seen to decrease quite rapidly with increasing benzene concentration to  $\epsilon_b \approx 0.1$ , after which the decrease is more gradual. The value plotted at  $\epsilon_b = 0.250$  is the upper limit of detection of 2,3-butanediol and no glycol was found in samples with  $\epsilon_b \geq 0.25$ .

c) Ethanol - 1,3-Pentadiene Solutions.

A second series of inhibition runs employing 1,3-pentadiene as the inhibitor was radiolyzed to a total dose of  $\approx 3.5 \times 10^{20}$  e.v./gm. at a dose rate of  $\approx 5 \times 10^{18}$  e.v./gm.-hr..

This compound was selected as a possible inhibitor for two reasons. Firstly, it was thought that a conjugated diene might act as an efficient trap for hydrogen atoms and other radicals. Secondly, preliminary chromatograms showed that the 1,3-pentadiene peak from the di-n-decyl phthalate column appeared where no interference with products from ethanol radiolysis would occur.

The data collected from these samples are presented as the dependence of  $G(\text{product})$  on  $\epsilon_p$ , the electron fraction of 1,3-pentadiene.

The measured products from ethanol radiolysis treated in this manner were hydrogen, methane, carbon monoxide, ethane, ethylene, propane, acetaldehyde (+ acetal) and 2,3-butanediol. A number of gas chromatographic peaks on the di-n-decyl phthalate column, that did not arise during pure ethanol radiolysis, were also measured. These



## FIGURE III-10

LIQUID PRODUCT YIELDS FROM THE RADIOLYSIS OF  
ETHANOL-BENZENE SOLUTIONS.

A. Acetaldehyde (and Acetal; see Table III-16)

 Average of two determinations.

B. 2,3-Butanediol

 Average of two determinations . Detection limit of glycol.Dashed lines represent  $G_X$ .

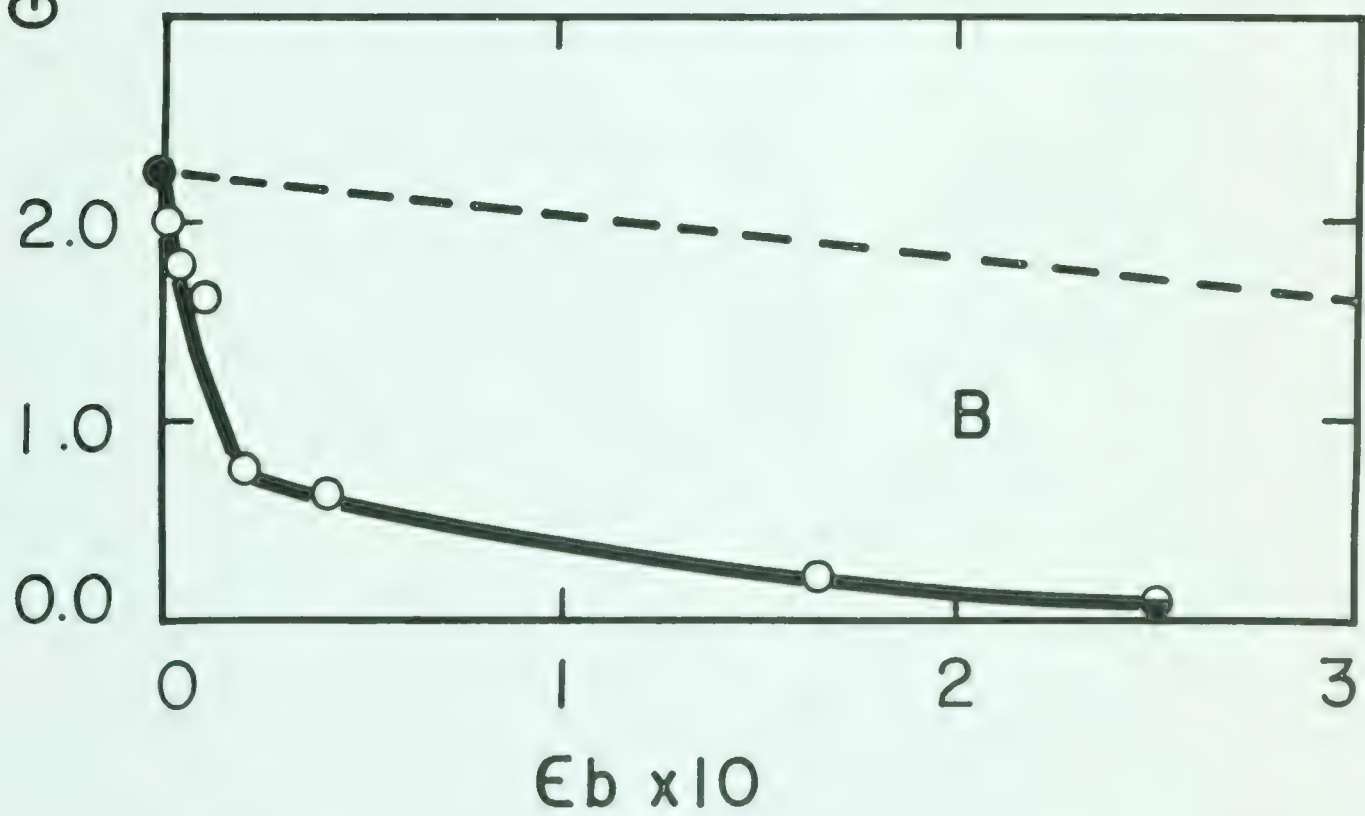
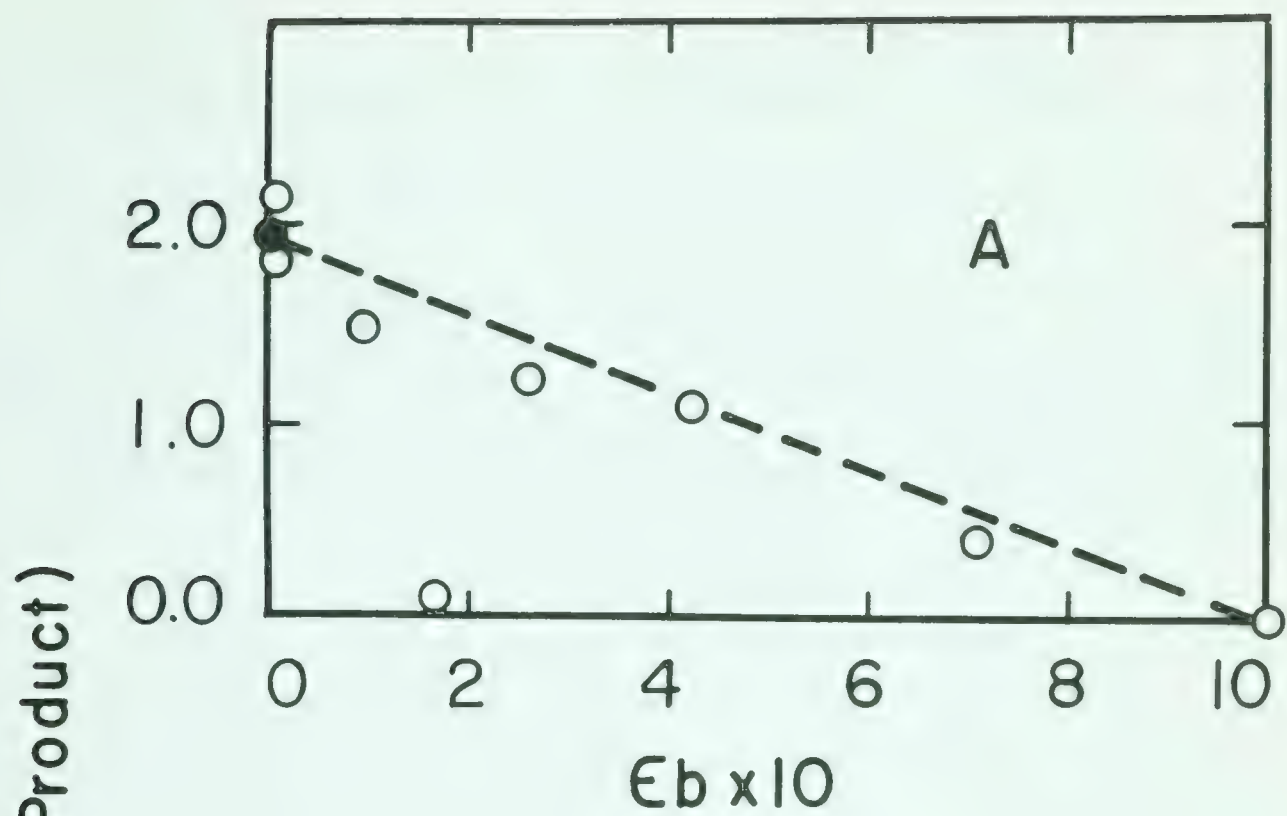




TABLE III-16

ACETALDEHYDE (AND ACETAL) YIELDS AS A FUNCTION OF  $\epsilon_b$ .

(Ethanol - Benzene Solution Radiolysis)

$\epsilon_b$	Total Dose e.v./gm.	G(Acetaldehyde)	G(Acetal)*	Total G(Acetalde- hyde Acetal)
0	$1.50 \times 10^{20}$	2.02	0.000	2.02
0	$1.49 \times 10^{20}$	1.85	0.026	1.88
$1.9 \times 10^{-3}$	$1.55 \times 10^{20}$	1.80	0.000	1.80
$5.0 \times 10^{-3}$	$1.49 \times 10^{20}$	0.16	1.970	2.13
$9.19 \times 10^{-2}$	$1.48 \times 10^{20}$	1.47	----	
0.165	$1.44 \times 10^{20}$	0.13	----	
0.250	$1.47 \times 10^{20}$	1.22	----	
0.421	$1.50 \times 10^{20}$	1.09	----	
0.708	$1.51 \times 10^{20}$	0.40		
1.000	$1.56 \times 10^{20}$	0.00		

Dose Rate =  $5 \times 10^{18}$  e.v./gm.-hr.\* Acetal could not be measured at benzene concentrations  $> \epsilon_b = 0.01$ .





TABLE III-17

2,3-BUTANEDIOL YIELD AS A FUNCTION OF  $\epsilon_b$ .

(Ethanol - Benzene Solution Radiolysis)

$\epsilon_b$	Total Dose e.v./gm.	G(2,3-Butanediol)
0	$1.50 \times 10^{20}$	2.30
0	$1.49 \times 10^{20}$	2.24
$1.9 \times 10^{-3}$	$1.55 \times 10^{20}$	2.00
$5.0 \times 10^{-3}$	$1.49 \times 10^{20}$	1.78
$1.04 \times 10^{-2}$	$1.49 \times 10^{20}$	1.66
$2.12 \times 10^{-2}$	$1.49 \times 10^{20}$	0.76
$4.16 \times 10^{-2}$	$1.49 \times 10^{20}$	0.65
0.165	$1.44 \times 10^{20}$	0.23
0.250	$1.47 \times 10^{20}$	$< 0.1^*$

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.

\* Limit of detection of glycol.



products were attributed to products possibly resulting from 1,3-pentadiene.

The dashed lines of the figures of this section represent the product yield to be expected if the alcohol and di-olefin were unaffected by the presence of each other during radiolysis.

a) Gaseous Products.

i) Hydrogen

Two graphs in Figure III-11 indicate the behavior of  $G(H_2)$  with varying  $\epsilon_p$ . The data for these plots are presented in Table III-18.

Figure III-11(A) shows  $G(H_2)$  at low values of  $\epsilon_p$  and is merely the sharply decreasing portion of Figure III-11(B) displayed on an extended  $\epsilon_p$  scale.

There appear to be two distinct regions to the curve. The first occurs between  $\epsilon_p = 0.00$  and about 0.05 in which  $G(H_2)$  decreases very sharply. From  $\epsilon_p \approx 0.05 - 1.0$  the decrease in  $G(H_2)$  is more gradual.

Comparison of Figure III-11 and Figure III-8(A) clearly shows that small amounts of 1,3-pentadiene have a more pronounced inhibitory effect than does benzene upon the production of hydrogen.

ii) Methane

The data for methane are presented in similar fashion as those for hydrogen. That is, Figure III-12(A) is the sharply decreasing segment of the curve of Figure III-12(B) displayed on a more revealing scale. The  $\epsilon_p$  boundaries for the two regions of the methane curve

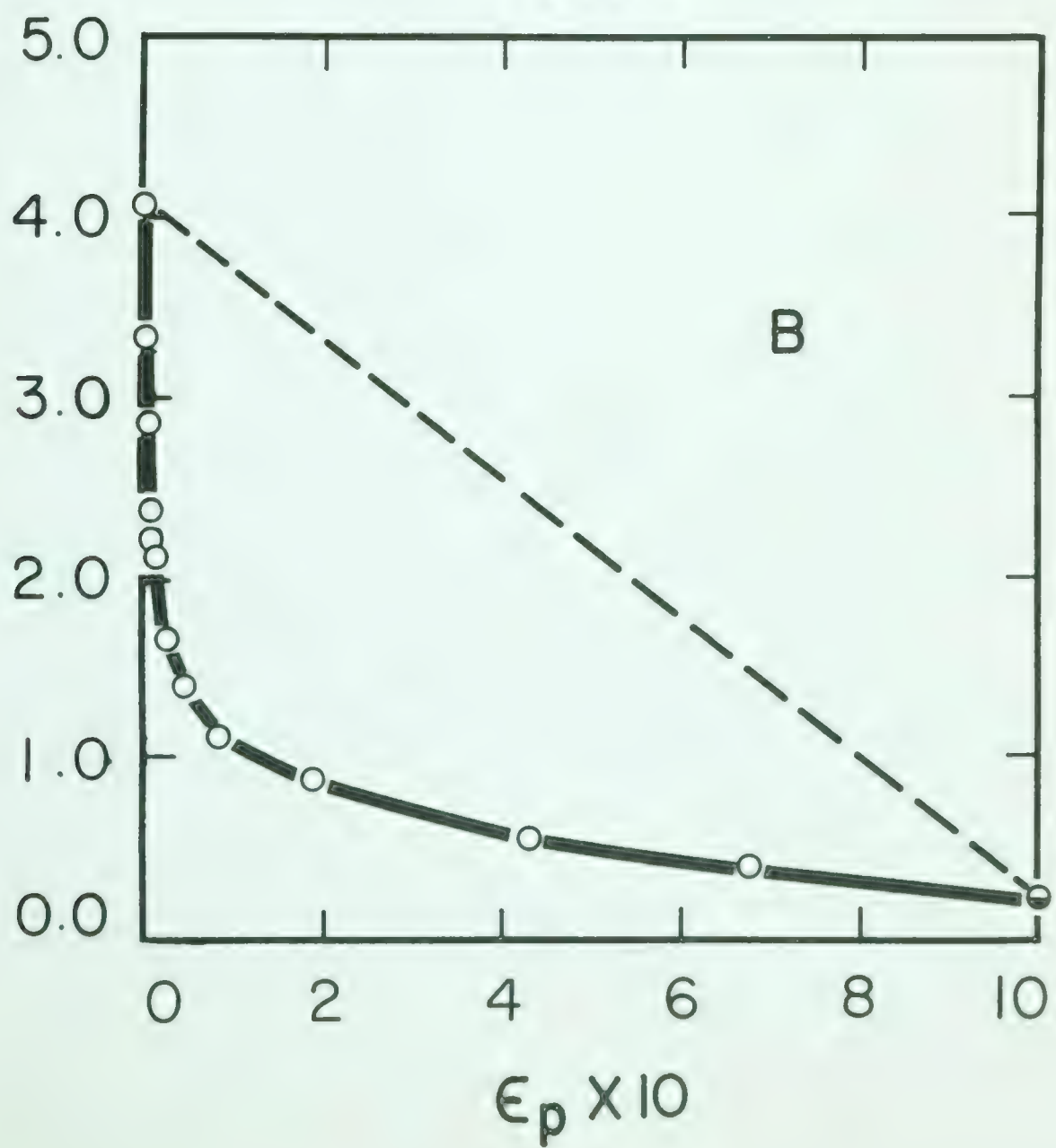
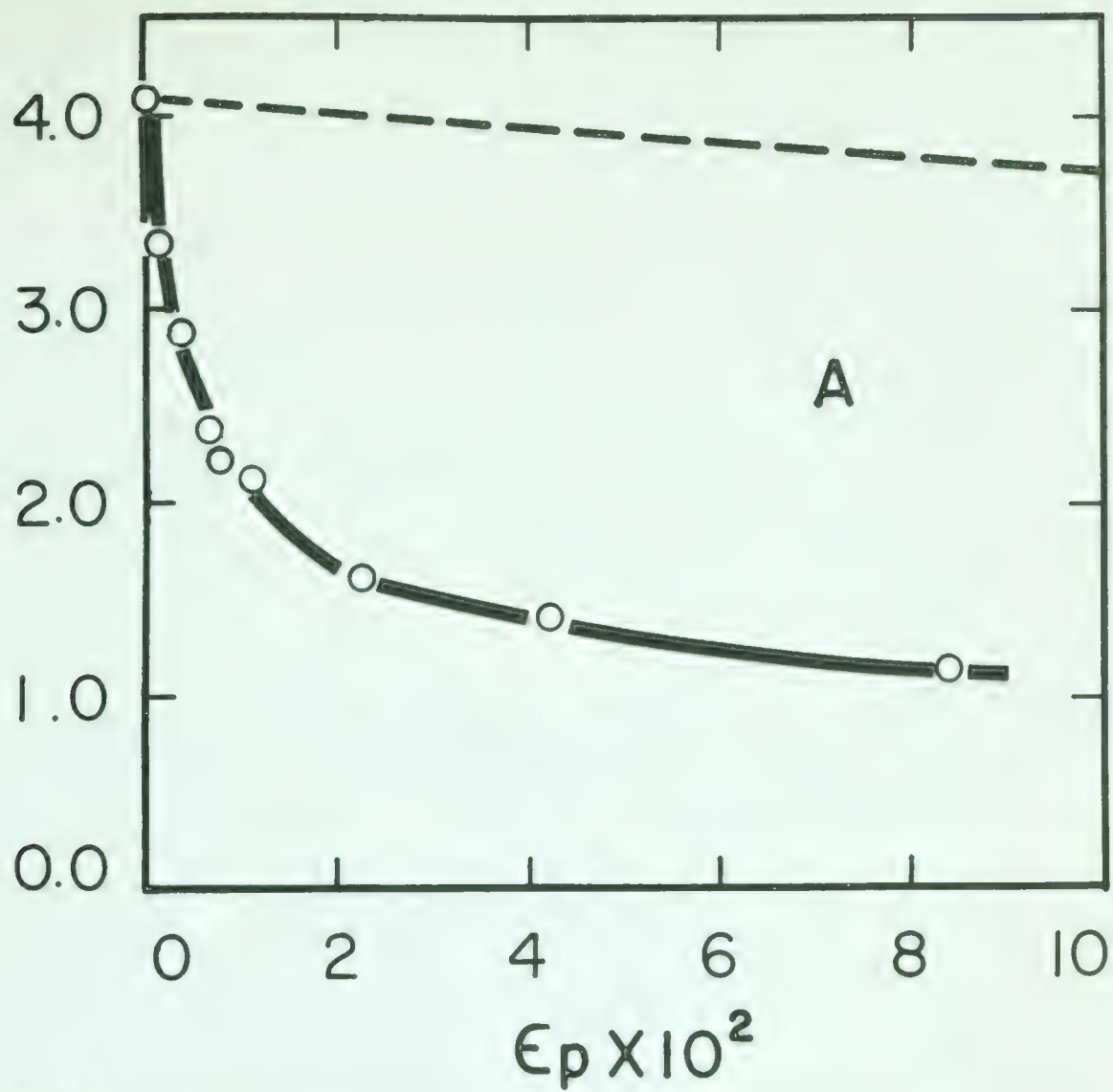
## FIGURE III-11

HYDROGEN YIELDS FROM THE RADIOLYSIS OF ETHANOL-  
1,3-PENTADIENE SOLUTIONS .

 Average of two determinations .

Dashed lines represent  $G_X$ .

$G(H_2)$





## FIGURE III-12

METHANE YIELDS FROM THE RADIOLYSIS OF ETHANOL-  
1,3-PENTADIENE SOLUTIONS.



Average of two values.

Dashed lines represent  $G_X$ .

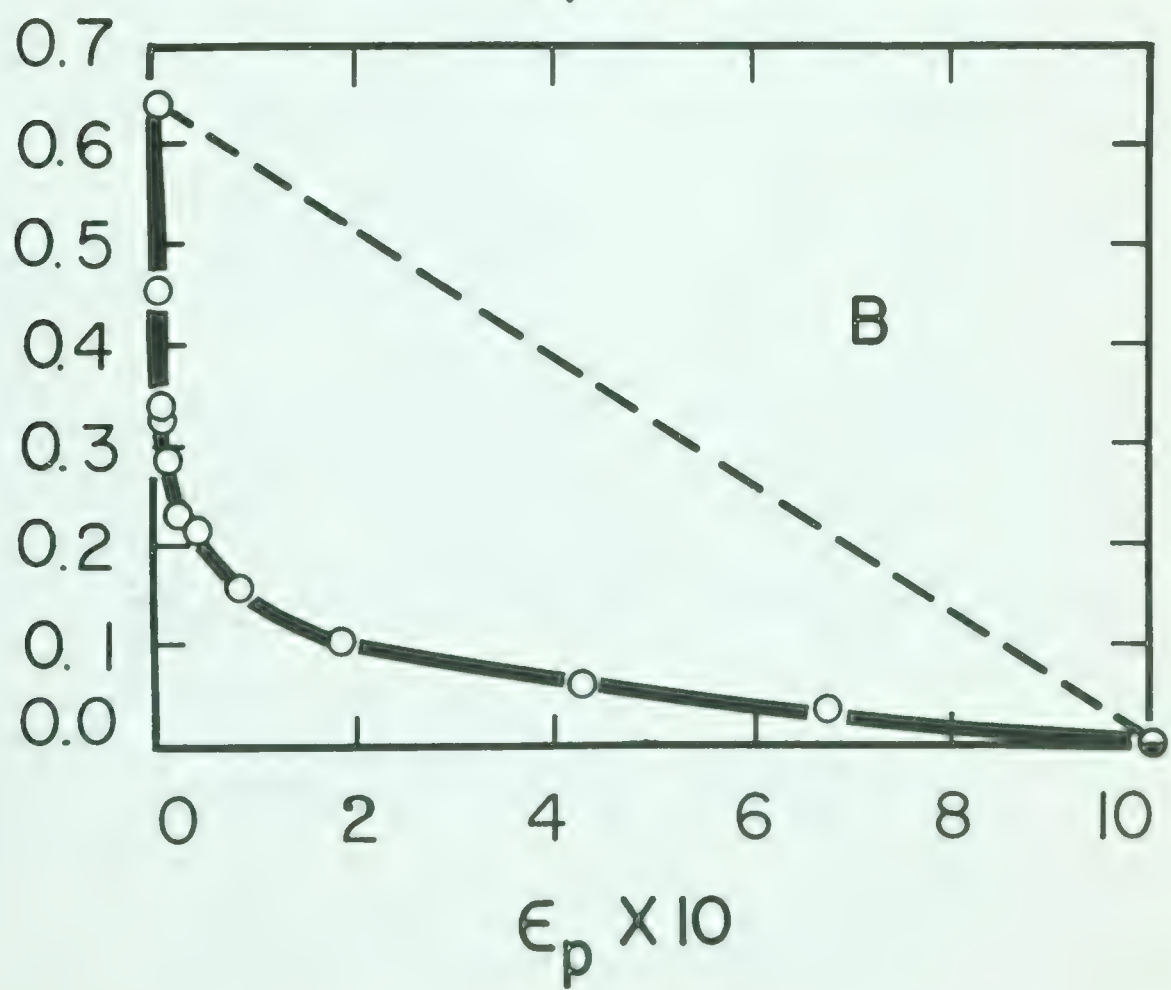
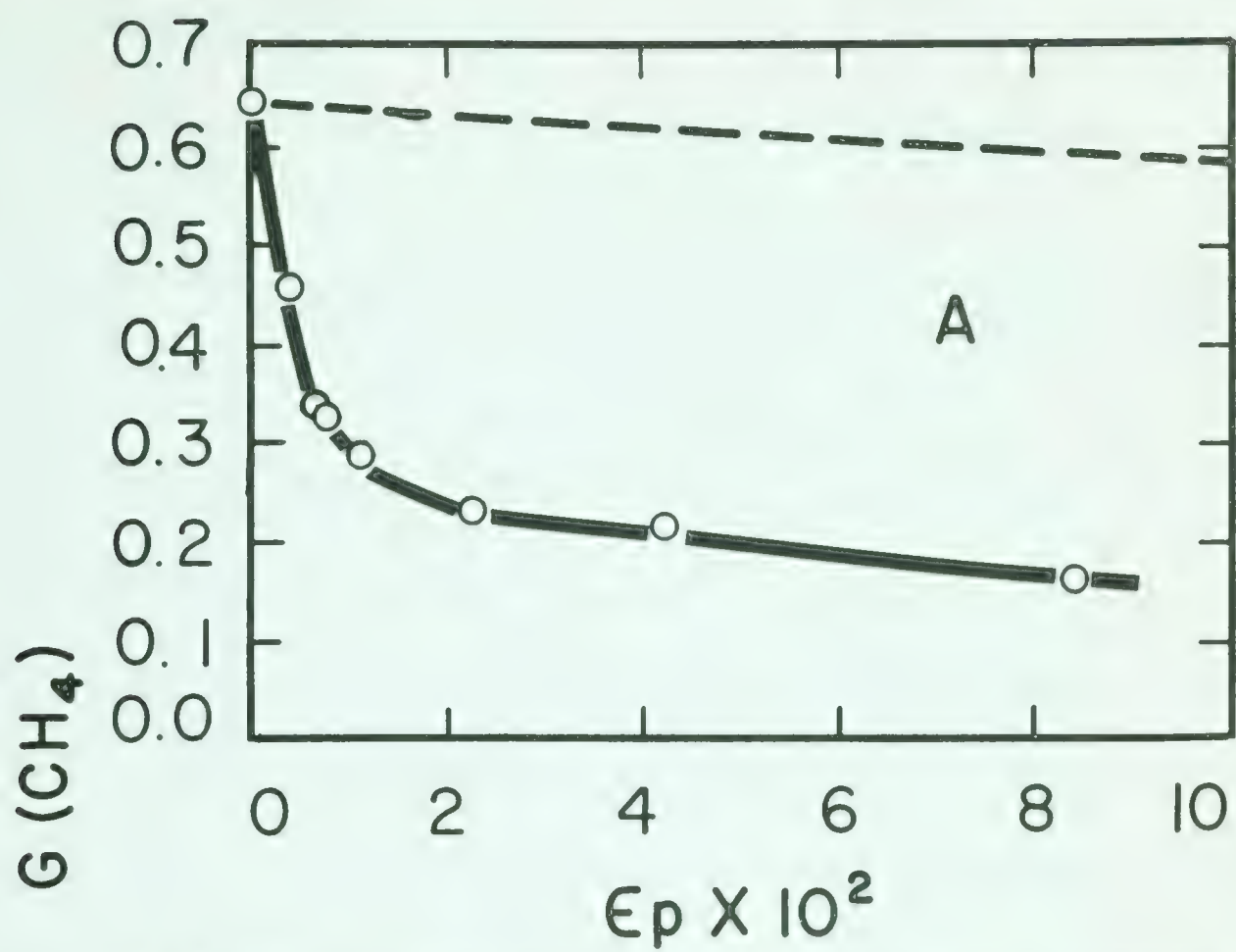




TABLE III-18

-196°C GAS FRACTION PRODUCT YIELDS AS A FUNCTION OF  $\epsilon_p$ .

(Ethanol-1,3-Pentadiene Solution Radiolysis)

$\epsilon_p$	Dose (e.v./gm.)	G(H <sub>2</sub> )	G(CH <sub>4</sub> )	G(CO)	G(-196°C)
1) 0	$3.49 \times 10^{20}$	4.08	0.645	0.053	4.78
2) $1.20 \times 10^{-3}$	$3.48 \times 10^{20}$	3.34	1.11	0.100	4.55
3) $3.84 \times 10^{-3}$	$3.50 \times 10^{20}$	2.87	0.456	0.048	3.37
4) $6.35 \times 10^{-3}$	$3.50 \times 10^{20}$	2.38	0.340	0.045	2.76
5) $7.89 \times 10^{-3}$	$3.50 \times 10^{20}$	2.22	0.325	0.050	2.60
6) $1.10 \times 10^{-2}$	$3.59 \times 10^{20}$	2.12	0.288	0.053	2.47
7) $2.25 \times 10^{-2}$	$3.50 \times 10^{20}$	1.66	0.230	0.042	1.94
8) $4.20 \times 10^{-2}$	$3.56 \times 10^{20}$	1.40	0.214	0.053	1.67
9) 0.084	$3.52 \times 10^{20}$	1.12	0.159	0.047	1.38
10) 0.187	$3.58 \times 10^{20}$	0.90	0.105	0.041	1.04
11) 0.428	$3.49 \times 10^{20}$	0.55	0.061	0.025	0.64
12) 0.672	$3.54 \times 10^{20}$	0.40	0.036	0.016	0.45
13) 1.000	$4.09 \times 10^{20}$	0.233	0.006	---	0.239
14) 1.000	$2.87 \times 10^{20}$	0.233	0.004	---	0.237

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.





appear to correspond to those for the hydrogen plots.

Comparison of Figure III-12 and Figure III-8(B) demonstrates that, as in the case of the hydrogen yield, 1,3-pentadiene is a more efficient inhibitor than is benzene for methane production. Table III-18 contains the data for the figure.

### iii) Carbon Monoxide

Figure III-13(A) and Table III-18 include the information gathered pertaining to the dependence of  $G(\text{CO})$  on  $\epsilon_p$ . The values are rather more scattered than those for hydrogen and methane, especially for low  $\epsilon_p$  samples. This was largely due to the fact that carbon monoxide constituted no more than 4% of the -196 fraction for any sample. Nevertheless, the values are reliable enough to show that 1,3-pentadiene has little or no effect upon the production of carbon monoxide from these samples, as opposed to its effect on the hydrogen and methane yields.

### iv) Ethane

The variation of the yield of ethane with the concentration of 1,3-pentadiene is displayed in Figure III-13(B). The numbers used to plot the figure are given in Table III-19. The plot shows the two regions corresponding to the regions discussed for hydrogen and methane.

### v) Ethylene

Figure III-13(C) and Table III-19 demonstrate the behaviour of  $G(\text{ethylene})$  with increasing amounts of 1,3-pentadiene. It can be seen that at low concentrations of di-olefin the ethylene increases to a maximum at  $\epsilon_p = 0.01$ , from which point a regular diminuation of

## FIGURE III-13

VARIOUS GASEOUS PRODUCT YIELDS FROM THE RADIOLYSIS  
OF ETHANOL-1,3-PENTADIENE SOLUTIONS.

A. Carbon Monoxide

B. Ethane

C. Ethylene

$G_X$  line drawn to  $G_i(\text{ethylene})$ .

D. Propane

Dash lines represent  $G_X$ .



Average of two determinations.



Yield at  $\epsilon_p = 0$ .

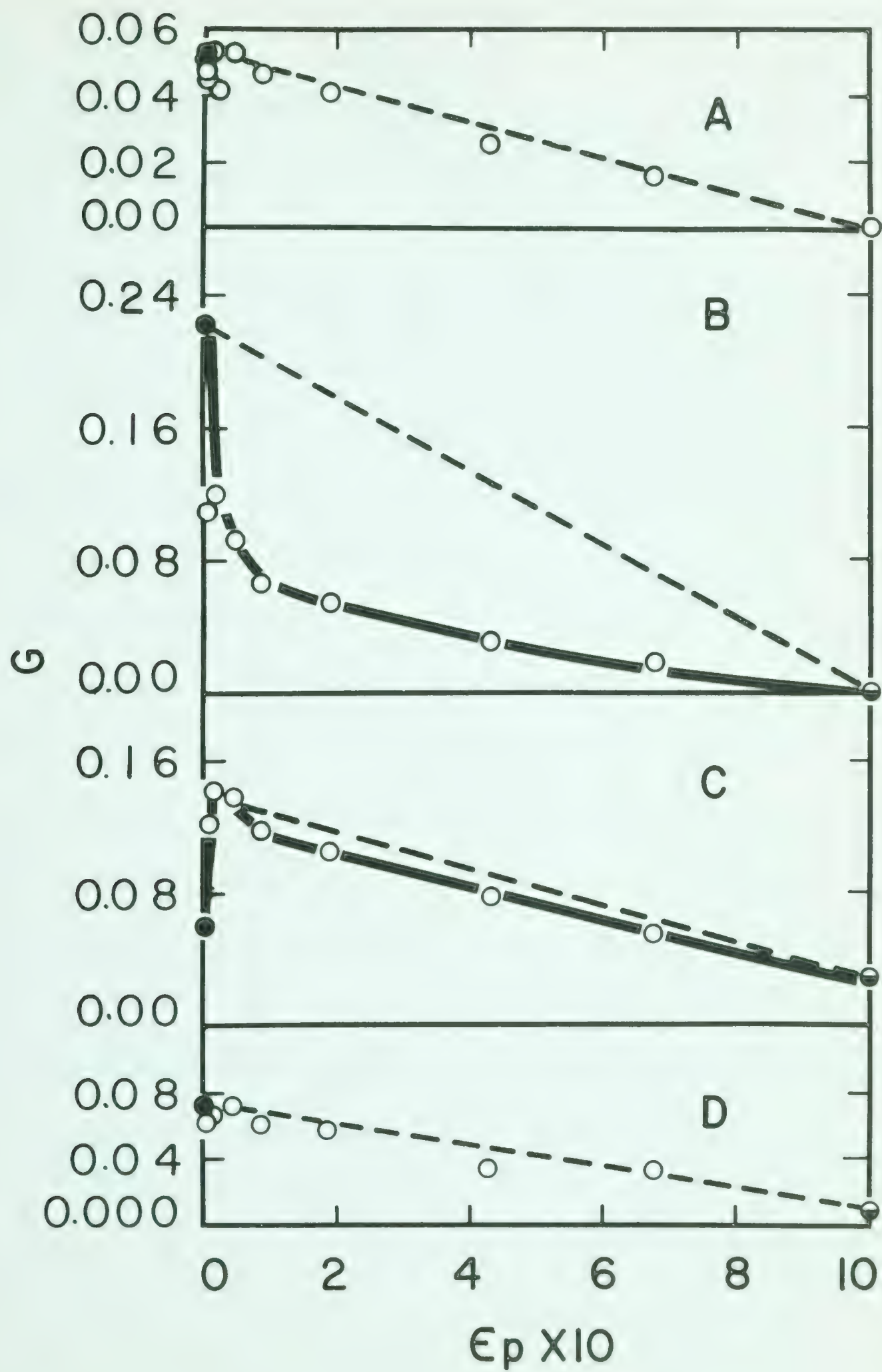




TABLE III-19

-112°C GAS FRACTION PRODUCT YIELDS AS A FUNCTION OF  $\epsilon_p$ .  
(Ethanol - 1,3-Pentadiene Solution Radiolysis)

$\epsilon_p$	Total Dose (e.v./gm.)	G(C <sub>2</sub> H <sub>6</sub> )	G(C <sub>2</sub> H <sub>4</sub> )	G(C <sub>3</sub> H <sub>8</sub> )
1) 0	3.49 x 10 <sup>20</sup>	0.222	0.060	0.0073
2) 7.89 x 10 <sup>-3</sup>	3.50 x 10 <sup>20</sup>	0.111	0.122	0.0063
3) 1.10 x 10 <sup>-2</sup>	3.59 x 10 <sup>20</sup>	0.120	0.142	0.0067
4) 4.20 x 10 <sup>-2</sup>	3.56 x 10 <sup>20</sup>	0.093	0.139	0.0073
5) 0.084	3.52 x 10 <sup>20</sup>	0.067	0.118	0.0062
6) 0.187	3.58 x 10 <sup>20</sup>	0.056	0.106	0.0058
7) 0.428	3.49 x 10 <sup>20</sup>	0.032	0.079	0.0035
8) 0.672	3.54 x 10 <sup>20</sup>	0.020	0.056	0.0034
9) 1.000	4.09 x 10 <sup>20</sup>	0.005	0.034	0.0020
10) 1.000	2.87 x 10 <sup>20</sup>	0.000	0.027	0.0000

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.





G(ethylene) occurs, to the value determined for pure 1,3-pentadiene radiolysis. It may be noticed that the G(ethylene) increase in the low  $\epsilon_p$  region of 0.08 G units is accompanied by a corresponding decrease yield of ethane.

vi) Propane

The variation of this minor product with di-olefin concentration is presented in Figure III-13(D) and Table III-19. Despite the scatter of the points it can be concluded that 1,3-pentadiene has a relatively small (if any) effect upon its production.

b) Liquid Products.

i) Acetaldehyde

The behavior of this product versus inhibitor concentration could be more reliably established with 1,3-pentadiene than with benzene, as acetal could be measured over the entire inhibitor concentration range. Figure III-14(A) and Table III-20 include the measurements obtained in this study. From the graph, it is observed that the combined yield of acetaldehyde (determined polarographically) plus the aldehyde present as acetal (determined by gas chromatography) follows the dashed line of G expected ( $G_X$ ) rather closely. Thus, it appears that both benzene and 1,3-pentadiene have insignificant effects upon the production of this product.

ii) 2,3-Butanediol

The second major liquid product from the radiolysis of liquid ethanol (2,3-butanediol) exhibited a vastly different behavior with di-olefin

## FIGURE III-14

ACETALDEHYDE (PLUS ACETAL) AND 2,3-BUTANEDIOL  
YIELDS FROM THE RADIOLYSIS OF ETHANOL-1,3-PENTA-  
DIENE SOLUTIONS.

## A. Acetaldehyde plus Acetal



Acetaldehyde plus acetal yield from pure  
liquid ethanol.

## B. 2,3-Butanediol



2,3-Butanediol yield from pure liquid  
ethanol.

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.

Dashed line represents  $G_X$ .

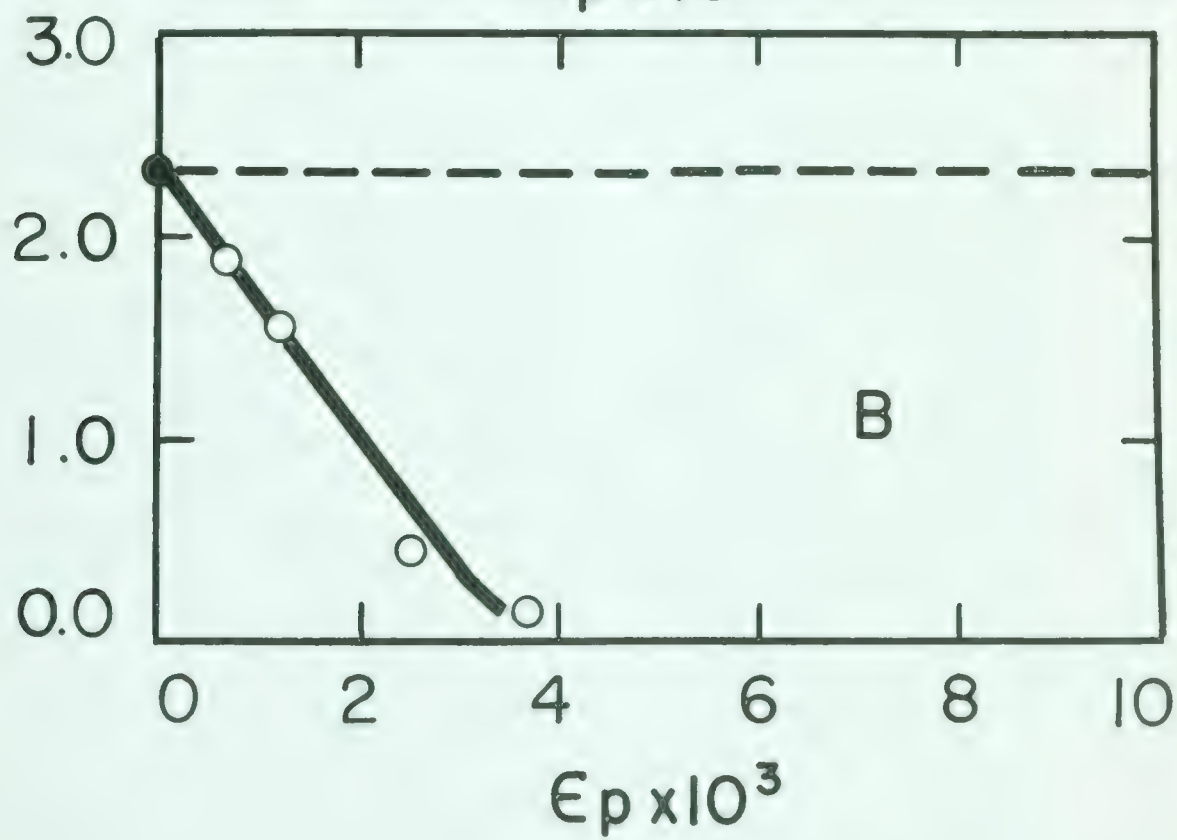
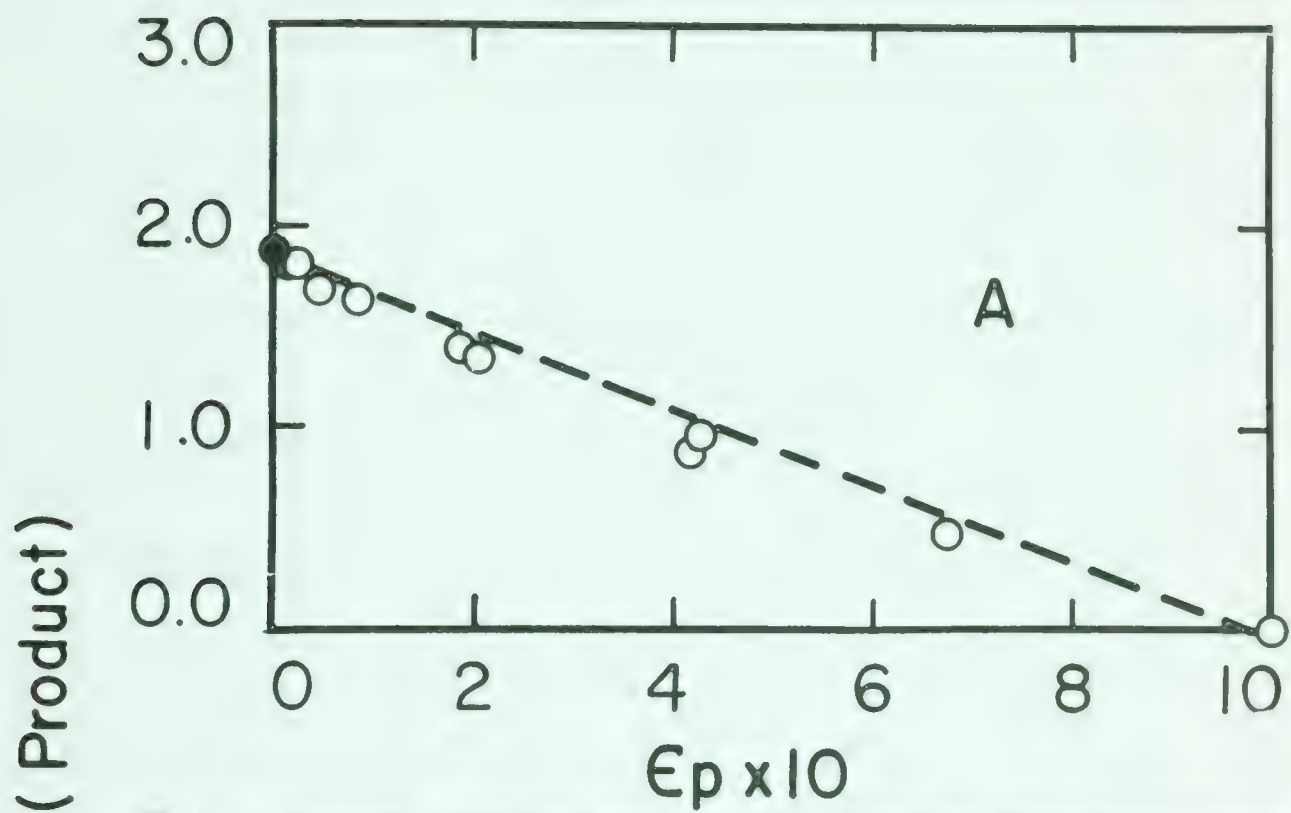






TABLE III-20

ACETALDEHYDE (PLUS ACETAL) YIELDS AS A FUNCTION OF  $\epsilon_p$ .

(Ethanol-1,3-Pentadiene Solution Radiolysis)

	$\epsilon_p$	Dose (e.v./gm.)	G(Acetaldehyde)	G(Acetal)	G(Acetalde- hyde plus Acetal)
1)	0	$3.49 \times 10^{20}$	1.665	0.21	1.88
2)	0.0012	$3.48 \times 10^{20}$	1.735	0.08	1.81
3)	0.0063	$3.50 \times 10^{20}$	1.72	0.00	1.72
4)	0.0110	$3.59 \times 10^{20}$	1.74	0.06	1.80
5)	0.0225	$3.50 \times 10^{20}$	1.735	0.07	1.81
6)	0.042	$3.56 \times 10^{20}$	1.55	0.135	1.69
7)	0.084	$3.52 \times 10^{20}$	1.45	0.19	1.64
8)	0.187	$3.58 \times 10^{20}$	1.27	0.13	1.40
9)	0.201	$3.50 \times 10^{20}$	1.23	0.12	1.35
10)	0.419	$3.50 \times 10^{20}$	0.80	0.09	0.89
11)	0.428	$3.49 \times 10^{20}$	0.88	0.09	0.97
12)	0.672	$3.54 \times 10^{20}$	0.45	0.03	0.48
13)	1.000	$4.09 \times 10^{20}$	--	--	--
14)	1.000	$2.87 \times 10^{20}$	--	--	--

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.



TABLE III-21

2,3-BUTANEDIOL YIELDS AS A FUNCTION OF  $\epsilon_p$ .

(Ethanol-1,3-Pentadiene Solution Radiolysis)

$\epsilon_p$		Dose (e.v./gm.)	G(2,3-Butanediol)
1)	0.00000	$3.49 \times 10^{20}$	2.34
2)	0.00062	$4.34 \times 10^{20}$	1.89
3)	0.00120	$3.48 \times 10^{20}$	1.55
4)	0.00250	$3.48 \times 10^{20}$	0.43
5)	0.00366	$3.47 \times 10^{20}$	0.14
6)	0.00384	$3.50 \times 10^{20}$	< 0.05*

\* Detection limit G(butanediol) &lt; 0.05.

Dose Rate  $\approx 5 \times 10^{18}$  e.v./gm.-hr.



concentration increase than did the aldehyde. Figure III-14(B) and Table III-21 display the extremely rapid disappearance of the glycol at very low 1,3-pentadiene concentrations. It was at first thought that manipulation in gas analysis procedures might have caused the glycol present to be lost for gas chromatographic analysis. However, supplementary binary mixtures of ethanol and 1,3-pentadiene, that were radiolyzed and subjected to liquid analysis by gas chromatography without prior gas analysis, showed no glycol present (within the detection limit of  $< 0.05$  G units), at the dose employed, above 1,3-pentadiene concentrations of  $\epsilon_p = 0.004$ . Hence, the observed extremely rapid disappearance of 2,3-butanediol at very low  $\epsilon_p$  was shown to result from true inhibition and not from faulty analytical technique.

### iii) Unidentified Liquid Products

A gas chromatographic peak was observed in the ethanol-1,3-pentadiene solutions that increased steadily with di-olefin concentration. The yields are plotted as peak area against  $\epsilon_p$ . In actual fact, this peak was separated into two distinct components at high pentadiene concentrations ( $\epsilon_p \gtrsim 0.5$ ). These poorly separated compounds are plotted as one peak in Figure III-15(A). (Data are tabulated in Table III-22). The behavior of peak area versus  $\epsilon_p$  suggests that this compounded peak is due to products derived from 1,3-pentadiene.

Two further peaks were measured, which displayed a different behavior with increasing di-olefin content. Numerical values are displayed in Figure III-15(B) and (C) and Table III-22. Using the same



## FIGURE III-15

UNIDENTIFIED LIQUID PRODUCT YIELDS FROM THE  
RADIOLYSIS OF ETHANOL-1,3-PENTADIENE SOLUTIONS.

- A. Yield of  $(a_1 + a_2)$  (unidentified products) as a  
function of  $\epsilon_p$ .
- B. Yield of  $b$  (unidentified product) as a function  
of  $\epsilon_p$ .
- C. Yield of  $c$  (unidentified product) as a function  
of  $\epsilon_p$ .

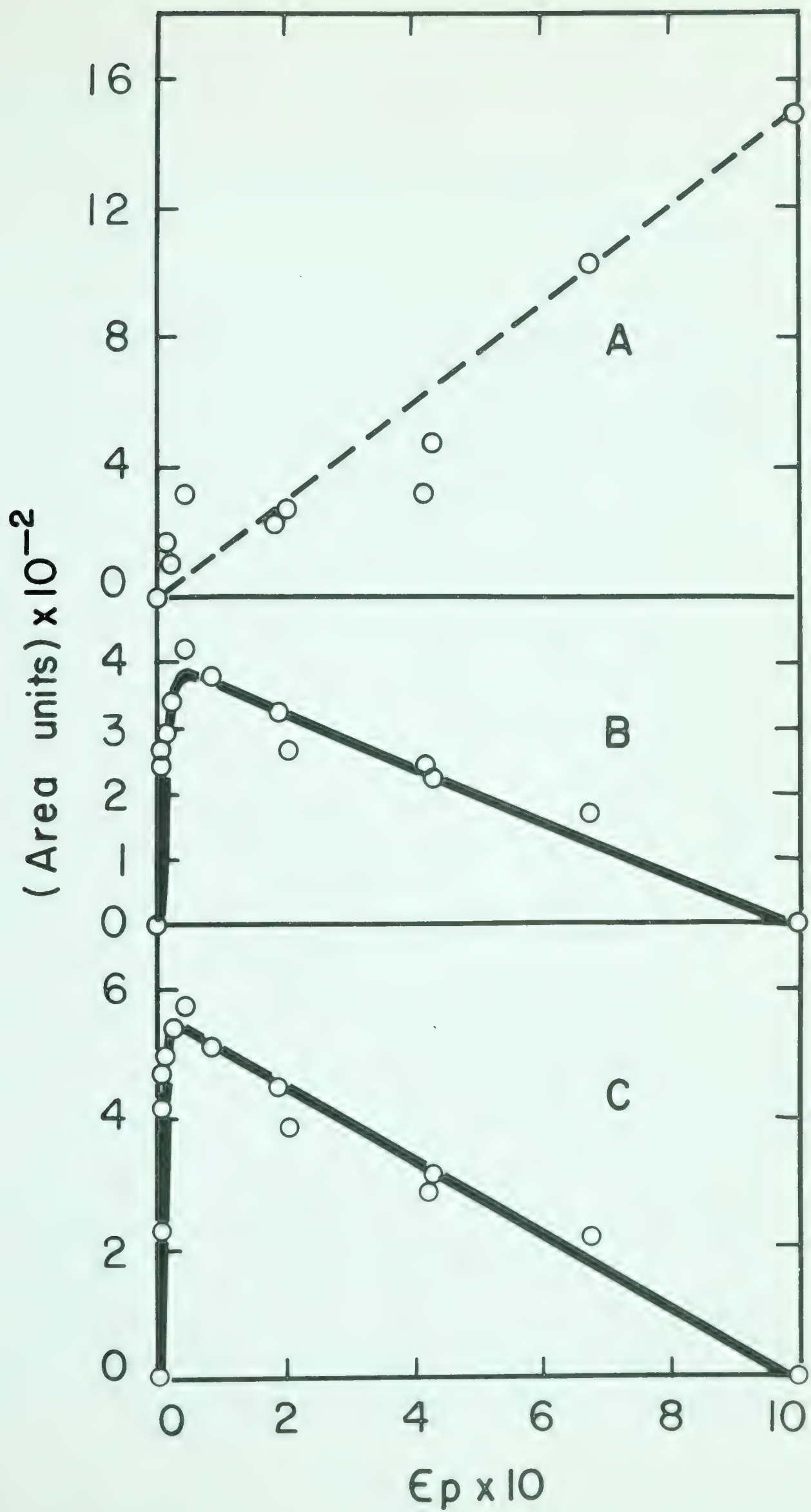




TABLE III-22

UNIDENTIFIED LIQUID PRODUCT YIELDS AS A FUNCTION OF  $\epsilon_p$ .

(Ethanol - 1,3-Pentadiene Solution Radiolysis)

$\epsilon_p$	Dose (e.v./gm.)	$a_1^*$	$a_2^*$	$a_1 + a_2^*$ $G_{max} \approx 1.8$	$b^*$ $G_{max} \approx 0.5$	$c^*$ $G_{max} \approx 0.7$
1) 0	$3.49 \times 10^{20}$	--	--	--	--	--
2) $3.84 \times 10^{-3}$	$3.50 \times 10^{20}$	--	--	--	--	228
3) $6.35 \times 10^{-3}$	$3.50 \times 10^{20}$	--	--	--	241	419
4) $7.89 \times 10^{-3}$	$3.50 \times 10^{20}$	--	--	--	267	472
5) $1.10 \times 10^{-2}$	$3.59 \times 10^{20}$	--	--	175	292	497
6) $2.25 \times 10^{-2}$	$3.50 \times 10^{20}$	--	--	102	341	543
7) $4.20 \times 10^{-2}$	$3.56 \times 10^{20}$	--	--	319	421	578
8) 0.084	$3.52 \times 10^{20}$	--	--	94	381	514
9) 0.187	$3.58 \times 10^{20}$	--	--	234	325	450
10) 0.201	$3.50 \times 10^{20}$	--	--	274	265	388
11) 0.419	$3.50 \times 10^{20}$	--	--	323	243	289
12) 0.428	$3.49 \times 10^{20}$	--	--	479	224	311
13) 0.672	$3.54 \times 10^{20}$	589	437	1026	170	218
14) 1.000	$4.09 \times 10^{20}$	1000	490	1490	0	0

\* The values listed in these columns are in arbitrary area units.

1500 area units = 2.3 G units of 2,3-butanediol at a dose of  $3.50 \times 10^{20}$  e.v./gm..





parameters as in Figure III-15(A), the yield of these two products were zero at zero concentration of 1,3-pentadiene, increased rapidly to a maximum at  $\epsilon_p \approx 0.04$  and then decreased gradually to zero for the pure 1,3-pentadiene samples.

This behavior was, at first, thought to indicate that these two peaks were due to "cross products" of ethanol and di-olefin. However, if these products were the result of a reaction of ethanol radicals with 1,3-pentadiene, it would be expected that the maximum yield of these products would occur at  $\epsilon_p = 0.004$  where the glycol yield disappeared. As the maximum values for both these peaks appear at  $\epsilon_p$  ten times greater than this, it is possible that, they are products arising from pentadiene. Justification for this premise will be outlined in the Discussion Section. Approximate G values for these products can be estimated from the graphs using the fact that 1500 area units  $\approx$  2.3 G units of 2,3-butanediol at the same dose ( $3.5 \times 10^{20}$  e.v./gm.).

The values of the products measured for pure ethanol samples in this set of runs lie reasonably close to the curves of the dose dependence graphs, with the exception of ethylene, in which case a dose rate dependence is indicated. Despite any discrepancy of the pure ethanol product yields from the aforementioned curves, the values exhibited by the alcohol-inhibitor samples are consistent within themselves, as they were all measured under identical conditions of all controllable parameters.



#### D. Deuterated Ethanol Samples.

The following isotopic alcohols were irradiated:  $\text{CD}_3\text{CD}_2\text{OD}$ ,  $\text{CH}_3\text{CH}_2\text{OD}$ ,  $\text{CD}_3\text{CD}_2\text{OH}$  (two separate sample lots from the supplier were investigated),  $\text{CH}_3\text{CD}_2\text{OH}$ , and  $\text{CD}_3\text{CH}_2\text{OH}$ . Light ethanol was also irradiated under the same conditions to act as a basis for comparison for the data collected from these compounds. Four different types of samples were prepared from each ethanol and subjected to  $\gamma$ -ray bombardment in the "Gamma cell 220" unit (dose rate  $\approx 6 \times 10^{19}$  e.v./gm.-hour).

The first type of sample was "pure" liquid ethanol, the word "pure" referring to the state in which the deuterated alcohol was received from Merck, Sharp and Dohme of Canada Ltd. The reasons for not attempting purification of the material supplied are outlined in the Experimental Section. In all cases analyses were performed on the alcohols to establish their isotopic and chemical purity. Table II-1 presents the results obtained from these analyses.

The second set of samples was radiolyzed in the gas phase at  $105 \pm 3^\circ \text{C}$ . The samples utilized approximately 0.8 gm. of the alcohol contained in a 500 ml. bulb, which resulted in a substrate pressure  $\approx 800$  mm. at  $105^\circ \text{C}$ . A summary of the yields obtained from the gas phase radiolysis of the light ethanol control runs is given in Table III-23. The values are the average of two determinations at a dose of  $3.3 \times 10^{20}$  e.v./cc. ( $4.1 \times 10^{20}$  e.v./gm.). The dose rate was approximately  $6 \times 10^{19}$  e.v./gm.-hour.



TABLE III-23

PRODUCT YIELDS FROM THE GAS PHASE  $\gamma$ -RADIOLYSIS OF ETHANOL

Product	G(Product)
Hydrogen	7.5
Methane	2.3
Carbon Monoxide	0.6
Ethane	0.2
Ethylene	1.2
Acetylene	0.09
Propane	0.01
Acetaldehyde	3.5
2,3-Butanediol	3.1
1,2-Propanediol	0.9





The third and fourth sets of samples were binary mixtures of alcohol and inhibitor (both liquid and gas phase). The results obtained from the previous inhibition studies indicated that 1,3-pentadiene would be a suitable inhibitor. Gas and liquid samples with pentadiene present were prepared with  $\epsilon_p = 0.200 \pm 0.011$ . At this concentration,  $G(\text{hydrogen})$  and  $G(\text{methane})$  for liquid samples were greatly reduced compared to the values for pure ethanol, and the variation of these yields with  $\epsilon_p$  in this region is gradual compared to the behavior at lower  $\epsilon_p$  ( $< 0.10$ ). (See Figures III-11 and III-12). Glycol yields for liquid samples with this amount of the di-olefin were below the detection limit at this dose (see Figure III-14). The gas phase ethanol-pentadiene mixtures had a pressure of  $\approx 1000$  mm..

The binary mixtures are referred to as "inhibited liquid" and "inhibited gas" samples, hereafter.

Liquid samples (both "pure" and "inhibited") were subjected to a dose of  $\approx 3.5 \times 10^{20}$  e.v./gm.. Both types of gaseous samples were dosed to  $\approx 4 \times 10^{20}$  e.v./gm..

The amount of alcohol used for each samples was measured as its liquid volume at  $0^\circ\text{C}$ . Merck, Sharp and Dohme of Canada Ltd. could provide no information concerning the density of the alcohols supplied. The only data discovered in the literature was that from a study of I. B. Rabinovich et al.<sup>(101)</sup> which included values of the density of  $\text{CH}_3\text{CH}_2\text{OD}$  at various temperatures. A graph of density versus temperature for  $\text{C}_2\text{H}_5\text{OD}$  is given in Figure III-16 while the data (taken

FIGURE III-16

DENSITY OF  $\text{C}_2\text{H}_5\text{OD}$  AS A FUNCTION OF

TEMPERATURE.

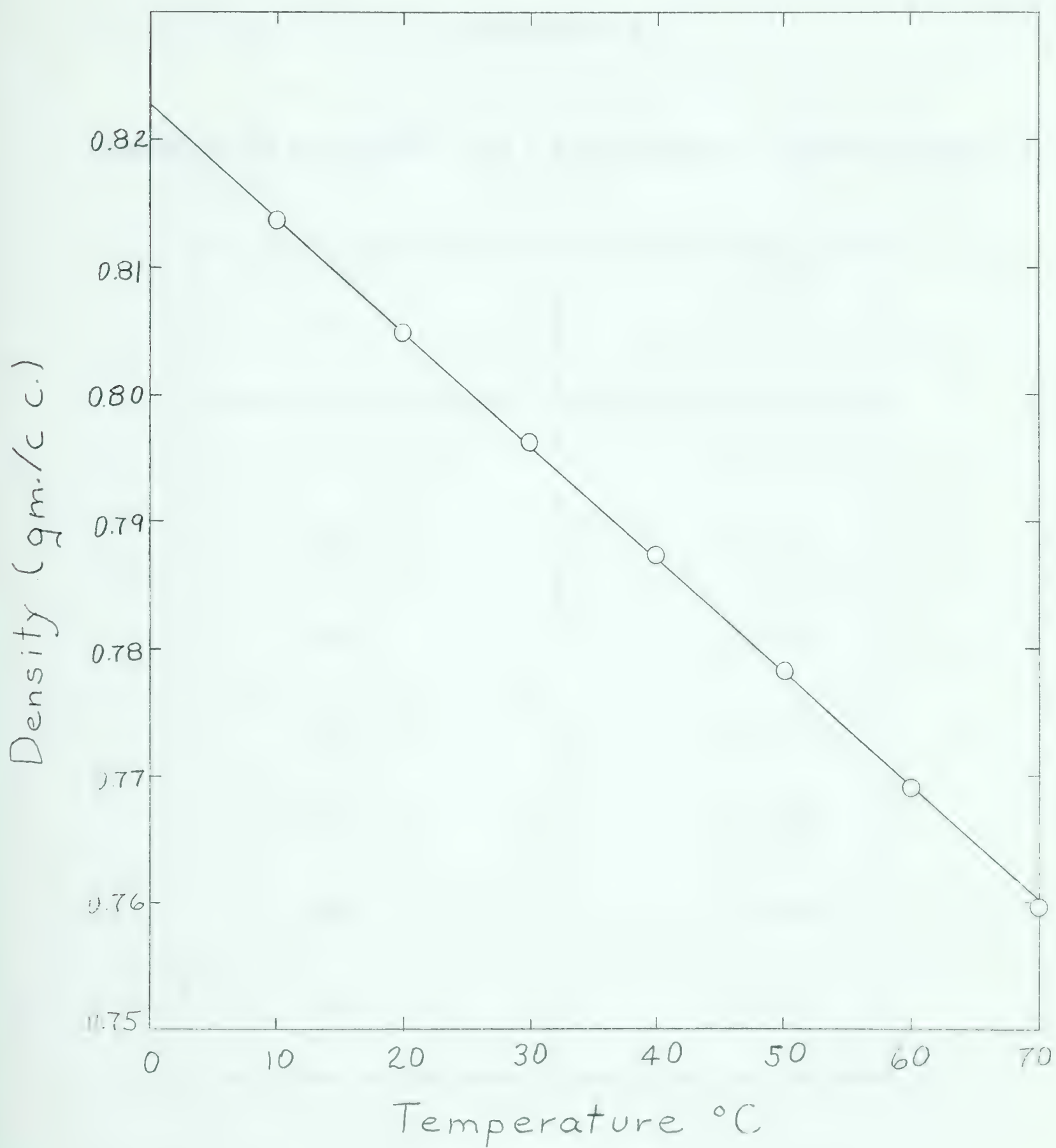






TABLE III-24

DENSITY OF  $\text{C}_2\text{H}_5\text{OD}^{(101)}$  AS A FUNCTION OF TEMPERATURE.

Temperature °C	Density (gm./cc.)
10	0.8137
20	0.8050
30	0.7964
40	0.7875
50	0.7784
60	0.7692
70	0.7597



from reference (101)) are shown in Table III-24. The line extrapolates to a density of 0.8227 (gm./cc.) at 0°C.

The density ratio of the -OD to the -OH ethanol

$$= \frac{0.8227}{0.8063} \text{ at } 0^\circ \text{C} = 1.02. \quad \text{The molecular weight ratio} = \frac{47.1}{46.1} = 1.02$$

Density data for heavy and light water at 25 C give a value of  $\frac{1.105}{0.997} =$

1.11. The molecular weight ratio  $= \frac{20.0}{18.0} = 1.11$ . These sets of ratios indicate that the density of isotopic compounds of this type increases in proportion to the molecular weight. This assumption was used to calculate the amount of alcohol present in the various samples investigated. As the number of molecules/cc. would be constant for all the alcohols, the absorbed doses are reported as e.v./cc. of liquid measured at 0°C, rather than as e.v./gm. as is usual.

#### a) Gaseous Products.

##### i) Hydrogen

The results pertaining to hydrogen production obtained for the pure liquid samples will be later compared to data concerning a similar investigation published by Burr<sup>(18)(64)</sup>. This study attempted to determine the relative importance of the three different possible sites of hydrogen production in the ethanol molecule. Mass spectrometric analyses for the H<sub>2</sub>, HD, and D<sub>2</sub> content of the radiolytic hydrogen provides useful information for this purpose.

Comparison of the amounts of these products from liquid and



gas phase samples of  $C_2H_5OD$  and  $C_2D_5OH$  should also provide evidence for any possible effect of hydrogen bonding upon hydrogen production.

$G(H_2)$ ,  $G(HD)$ ,  $G(D_2)$ , and  $G(\text{Total Hydrogen})$  are tabulated in Tables III-25 and III-26 for liquid and gaseous ethanol and ethanol-1,3-pentadiene mixtures (both light and deuterated ethanols).

Unfortunately, the presence of various impurities in the alcohols seems to have affected some of the hydrogen results. Thus the high value for  $G(\text{total hydrogen})$  for the liquid  $C_2H_5OD$  sample is most probably due to a small amount of acid in the alcohol. Similarly, the large difference in the amount of hydrogen obtained from two separate samples of  $C_2D_5OD$  from Merck, Sharp and Dohme is undoubtedly caused by the different natures and amounts of impurities contained in the two lots. Despite these drawbacks pertinent facts could be obtained from the numbers in Tables III-25 and III-26. The samples containing the 1,3-pentadiene were useful in providing information as to mode and probable sites of hydrogen production.

The per cent deuterium contained in the hydrogen from deuterated substrate was determined

$$\%D = \frac{(G(D_2) + 1/2 G(HD)) \times 100}{G(\text{Total Hydrogen})}$$

and is contained in Table III-27.

Theoretically there should have been 100% deuterium in the hydrogen derived from  $CD_3CD_2OD$ . In fact, there was only 97% D for these samples. Isotopic analysis of the  $C_2D_5OD$  (Table II-1) would drop





TABLE III-25

HYDROGEN YIELDS FROM THE RADIOLYSIS OF LIQUID ETHANOL  
AND LIQUID ETHANOL-1,3-PENTADIENE SOLUTIONS (LIGHT AND  
DEUTERATED ALCOHOLS).

Alcohol	$\epsilon_p$	Dose (e.v./cc.)	G(H <sub>2</sub> )	G(HD)	G(D <sub>2</sub> )	G(Total Hydrogen)
CH <sub>3</sub> CH <sub>2</sub> OH	.0	2.82 x 10 <sup>20</sup>	4.20	--	--	4.20
CH <sub>3</sub> CH <sub>2</sub> OH	0	2.84 x 10 <sup>20</sup>	4.27	--	--	4.27
CD <sub>3</sub> CD <sub>2</sub> OD	0	2.76 x 10 <sup>20</sup>	0.03	0.14	3.10	3.27
CH <sub>3</sub> CH <sub>2</sub> OD	0	2.80 x 10 <sup>20</sup>	1.62	3.45	0.08	5.15
CD <sub>3</sub> CD <sub>2</sub> OH <sup>1)</sup>	0	2.74 x 10 <sup>20</sup>	0.33	1.94	0.69	2.96
CD <sub>3</sub> CD <sub>2</sub> OH <sup>2)</sup>	0	2.82 x 10 <sup>20</sup>	0.59	2.62	0.77	3.97
CH <sub>3</sub> CD <sub>2</sub> OH	0	2.88 x 10 <sup>20</sup>	0.84	1.68	0.32	2.84
CD <sub>3</sub> CH <sub>2</sub> OH	0	2.86 x 10 <sup>20</sup>	3.00	0.40	0.04	3.44
CH <sub>3</sub> CH <sub>2</sub> OH	0.204	2.79 x 10 <sup>20</sup>	0.88	--	--	0.88
CH <sub>3</sub> CH <sub>2</sub> OH	0.198	2.80 x 10 <sup>20</sup>	0.89	--	--	0.89
CD <sub>3</sub> CD <sub>2</sub> OD	0.193	2.75 x 10 <sup>20</sup>	0.06	0.11	0.40	0.57
CH <sub>3</sub> CH <sub>2</sub> OD	0.192	2.77 x 10 <sup>20</sup>	0.65	0.20	0.01	0.86
CD <sub>3</sub> CD <sub>2</sub> OH	0.208	2.74 x 10 <sup>20</sup>	0.17	0.32	0.13	0.62
CH <sub>3</sub> CD <sub>2</sub> OH	0.209	2.84 x 10 <sup>20</sup>	0.34	0.31	0.06	0.71
CD <sub>3</sub> CH <sub>2</sub> OH	0.188	2.84 x 10 <sup>20</sup>	0.65	0.15	0.02	0.82

1), 2) Two separate sample lots from Merck, Sharp and  
Dohme of Canada Ltd..



TABLE III-26

HYDROGEN YIELDS FROM THE RADIOLYSIS OF GASEOUS ETHANOL  
AND GASEOUS ETHANOL-1,3-PENTADIENE MIXTURES (LIGHT AND  
DEUTERATED ETHANOLS).

Alcohol	$\epsilon$ p	Dose (e.v./cc.)	G(H <sub>2</sub> )	G(HD)	G(D <sub>2</sub> )	G(Total Hydrogen)
CH <sub>3</sub> CH <sub>2</sub> OH	0	3.32 x 10 <sup>20</sup>	7.51	--	--	7.51
CH <sub>3</sub> CH <sub>2</sub> OH	0	3.32 x 10 <sup>20</sup>	7.40	--	--	7.40
CD <sub>3</sub> CD <sub>2</sub> OD	0	3.14 x 10 <sup>20</sup>	0.07	0.32	6.53	6.92
CH <sub>3</sub> CH <sub>2</sub> OD	0	3.14 x 10 <sup>20</sup>	4.19	2.60	0.19	6.98
CD <sub>3</sub> CD <sub>2</sub> OH <sup>1)</sup>	0	6.51 x 10 <sup>20</sup>	0.16	1.35	2.24	3.75
CD <sub>3</sub> CD <sub>2</sub> OH <sup>2)</sup>	0	3.11 x 10 <sup>20</sup>	0.43	2.50	2.70	5.63
CH <sub>3</sub> CD <sub>2</sub> OH	0	3.10 x 10 <sup>20</sup>	0.90	2.08	1.12	4.10
CD <sub>3</sub> CH <sub>2</sub> OH	0	3.06 x 10 <sup>20</sup>	3.92	0.97	0.17	5.06
CH <sub>3</sub> CH <sub>2</sub> OH	0.191	3.17 x 10 <sup>20</sup>	1.38	--	--	1.38
CH <sub>3</sub> CH <sub>2</sub> OH	0.198	3.15 x 10 <sup>20</sup>	1.49	--	--	1.49
CD <sub>3</sub> CD <sub>2</sub> OD	0.204	3.00 x 10 <sup>20</sup>	0.11	0.12	0.69	0.92
CH <sub>3</sub> CH <sub>2</sub> OD	0.194	3.04 x 10 <sup>20</sup>	1.03	0.34	0.009	1.38
CD <sub>3</sub> CD <sub>2</sub> OH	0.194	3.04 x 10 <sup>20</sup>	0.23	0.28	0.43	0.94
CH <sub>3</sub> CD <sub>2</sub> OH	0.199	3.01 x 10 <sup>20</sup>	0.45	0.27	0.12	0.84
CD <sub>3</sub> CH <sub>2</sub> OH	0.189	2.95 x 10 <sup>20</sup>	0.74	0.23	0.12	1.09

1), 2) Two separate sample lots. from Merck, Sharp and Dohme  
of Canada Ltd..





TABLE III-27

PER CENT DEUTERIUM IN THE RADIOLYTIC HYDROGEN FROM  
DEUTERATED ETHANOLS AND ETHANOL-1,3-PENTADIENE  
MIXTURES.

Alcohol	Pure Liquid	Pure Gas	Inhibited Liquid	Inhibited Gas
$\text{CH}_3\text{CH}_2\text{OD}$	35.0	21.3	12.8	13.0
$\text{CD}_3\text{CD}_2\text{OH}$ 1st Sample	56.1	77.8	46.7	60.6
$\text{CD}_3\text{CD}_2\text{OH}$ 2nd Sample	52.3	70.0	--	--
$\text{CH}_3\text{CD}_2\text{OH}$	40.8	52.9	30.1	30.7
$\text{CD}_3\text{CH}_2\text{OH}$	6.9	13.1	11.6	21.6
$\text{CD}_3\text{CD}_2\text{OD}$	97.0	96.4	80.5	82.1



TABLE III-28

PERCENT  $H_2$ , HD, AND  $D_2$  IN THE RADIOLYTIC HYDROGEN FROM  
DEUTERATED ALCOHOLS.

Alcohol	Sample	% $H_2$	% HD	% $D_2$
$CD_3CD_2OD$	pure liquid	0.9	4.3	94.9
$CH_3CH_2OD$	pure liquid	31.4	67.0	1.6
$CD_3CD_2OH$	pure liquid	11.2	65.5	23.3
$CD_3CD_2OH$	pure liquid	14.8	66.0	19.4
$CH_3CD_2OH$	pure liquid	29.6	59.1	11.3
$CD_3CH_2OH$	pure liquid	87.1	11.6	1.2
$CD_3CD_2OD$	inhibited liquid	10.5	19.3	70.3
$CH_3CH_2OD$	inhibited liquid	75.5	23.2	1.2
$CD_3CD_2OH$	inhibited liquid	27.4	51.6	21.0
$CH_3CD_2OH$	inhibited liquid	47.8	43.6	8.5
$CD_3CH_2OH$	inhibited liquid	79.2	18.3	2.4
$CD_3CD_2OD$	pure gas	1.1	4.6	94.3
$CH_3CH_2OD$	pure gas	60.0	37.2	2.7
$CD_3CD_2OH$	pure gas	4.3	36.0	59.7
$CD_3CD_2OH$	pure gas	7.6	44.4	48.0
$CH_3CD_2OH$	pure gas	22.0	50.7	27.3
$CD_3CH_2OH$	pure gas	77.4	19.2	3.4
$CD_3CD_2OD$	inhibited gas	12.0	13.0	75.0
$CH_3CH_2OD$	inhibited gas	74.7	24.6	0.7
$CD_3CD_2OH$	inhibited gas	24.5	29.8	45.8
$CH_3CD_2OH$	inhibited gas	53.5	32.1	14.3
$CD_3CH_2OH$	inhibited gas	67.9	21.1	11.0



this to  $\leq 99.5\%$  deuterium. The low figure actually observed could reflect an isotope effect or errors introduced by mass spectrometric analytical manipulations. Burr's results for  $C_2D_5OD$  also exhibited this type of discrepancy.

The hydrogen analyses are also presented as percent  $H_2$ ,  $HD$ , and  $D_2$  in the radiolytic hydrogen (Table III-28) to reveal any further correlations and trends.

Significant facts gleaned from these tables will be summarized and commented upon in the Discussion Section.

ii) Methane

Tables III-29 and III-30 display methane yields for liquid and gaseous samples of light and deuterated ethanol and ethanol-inhibitor binary mixtures.

The same limitations caused by impurities concerning data accuracy apply to these numbers as to those concerning hydrogen.

iii) Carbon Monoxide

Carbon monoxide yields from these samples are displayed in Table III-31. The liquid phase G values are very scattered due to small amount present, combined with the necessity of subtracting a blank nitrogen correction from the observed yield. This air was from the mass spectrometer background blank and a small amount ( $< 1\%$ ) of air introduced by gas analysis manipulations. This correction was not necessary for the results obtained by gas chromatography and more reliable carbon monoxide yields were obtained in the earlier sets of





TABLE III-29

METHANE YIELDS FROM THE RADIOLYSIS OF LIQUID ETHANOL AND ETHANOL-1,3-PENTADIENE SOLUTIONS (LIGHT AND DEUTERATED ALCOHOLS).

Alcohol	$\epsilon_p$	G(CH <sub>4</sub> )	G(CH <sub>3</sub> D)	G(CH <sub>2</sub> D <sub>2</sub> )	G(CHD <sub>3</sub> )	G(CD <sub>4</sub> )	G(Total Methane)
CH <sub>3</sub> CH <sub>2</sub> OH	0	0.52	--	--	--	--	0.52 } Avg. 0.49 0.46 } 0.41 } 0.56 }
CH <sub>3</sub> CH <sub>2</sub> OH	0	0.46	--	--	--	--	
CD <sub>3</sub> CD <sub>2</sub> OD	0	--	--	0.03	0.03	0.35	
CH <sub>3</sub> CH <sub>2</sub> OD	0	0.48	0.08	--	--	--	
CD <sub>3</sub> CD <sub>2</sub> OH <sup>1)</sup>	0	--	--	0.03	0.11	0.13	0.27
CD <sub>3</sub> CD <sub>2</sub> OH <sup>2)</sup>	0	--	--	0.03	0.16	0.31	0.50
CH <sub>3</sub> CD <sub>2</sub> OH	0	0.26	0.21	--	--	--	0.47
CD <sub>3</sub> CH <sub>2</sub> OH	0	--	--	0.08	0.47	0.02	0.57
CH <sub>3</sub> CH <sub>2</sub> OH	0.204	0.08	--	--	--	--	0.08 } Avg. 0.08 0.08 } 0.08 } 0.10 }
CH <sub>3</sub> CH <sub>2</sub> OH	0.198	0.08	--	--	--	--	
CD <sub>3</sub> CD <sub>2</sub> OD	0.193	--	--	0.005	0.01	0.06	
CH <sub>3</sub> CH <sub>2</sub> OD	0.192	0.08	0.02	--	--	--	
CD <sub>3</sub> CD <sub>2</sub> OH	0.208	--	--	0.006	0.03	0.04	0.08
CH <sub>3</sub> CD <sub>2</sub> OH	0.209	0.06	0.05	--	--	--	0.11
CD <sub>3</sub> CH <sub>2</sub> OH	0.188	--	--	0.01	0.08	0.007	0.10

1), 2) Separate sample lots from Merck, Sharp and Dohme of Canada Ltd..

Doses are the same as those of Table III-24 for corresponding samples.



TABLE III-30

METHANE YIELDS FROM THE RADIOLYSIS OF GASEOUS ETHANOL AND ETHANOL-1,3-PENTADIENE MIXTURES (LIGHT AND DEUTERATED ALCOHOLS).

Alcohol	$\epsilon_p$	G(CH <sub>4</sub> )	G(CH <sub>3</sub> D)	G(CH <sub>2</sub> D <sub>2</sub> )	G(CHD <sub>3</sub> )	G(CD <sub>4</sub> )	G(Total Methane)
CH <sub>3</sub> CH <sub>2</sub> OH	0	2.25	--	--	--	--	2.25 } Avg. 2.30
CH <sub>3</sub> CH <sub>2</sub> OH	0	2.34	--	--	--	--	2.34 }
CD <sub>3</sub> CD <sub>2</sub> OD	0	--	--	0.04	0.13	1.38	1.54
CH <sub>3</sub> CH <sub>2</sub> OD	0	2.44	0.24	--	--	--	2.68
CD <sub>3</sub> CD <sub>2</sub> OH <sup>1)</sup>	0	--	--	0.03	0.14	0.19	0.36
CD <sub>3</sub> CD <sub>2</sub> OH <sup>2)</sup>	0	--	--	0.14	0.90	1.19	2.23
CH <sub>3</sub> CD <sub>2</sub> OH	0	0.48	0.34	0.02	--	--	0.84
CD <sub>3</sub> CH <sub>2</sub> OH	0	--	--	0.26	1.31	0.03	1.60
CH <sub>3</sub> CH <sub>2</sub> OH	0.191	0.23	--	--	--	--	0.23 } Avg. 0.22
CH <sub>3</sub> CH <sub>2</sub> OH	0.198	0.21	--	--	--	--	0.21 }
CD <sub>3</sub> CD <sub>2</sub> OD	0.204	--	--	0.02	0.04	0.13	0.19
CH <sub>3</sub> CH <sub>2</sub> OD	0.194	0.22	0.05	--	--	--	0.27
CD <sub>3</sub> CD <sub>2</sub> OH	0.194	--	--	0.01	0.07	0.10	0.18
CH <sub>3</sub> CD <sub>2</sub> OH	0.199	0.11	0.08	0.005	--	--	0.20
CD <sub>3</sub> CH <sub>2</sub> OH	0.189	--	--	--	0.24	0.01	0.25

1), 2) Separate sample lots from Merck, Sharp and Dohme of Canada Ltd..

Doses are the same as those of Table III-25 for corresponding samples.





TABLE III-31

CARBON MONOXIDE YIELDS FROM THE RADIOLYSIS OF ETHANOL  
AND ETHANOL-1,3-PENTADIENE MIXTURES (LIGHT AND  
DEUTERATED ALCOHOLS).

Alcohol	Liquid		Gas		G(CO)inhibited
	$\epsilon_p$	G(CO)	$\epsilon_p$	G(CO)	G(CO)pure
CH <sub>3</sub> CH <sub>2</sub> OH	0	0.02	0	0.58	0.49
CH <sub>3</sub> CH <sub>2</sub> OH	0	0.06	0	0.60	
CD <sub>3</sub> CD <sub>2</sub> OD	0	0.00	0	0.43	0.60
CH <sub>3</sub> CH <sub>2</sub> OD	0	0.03	0	0.93	0.31
CD <sub>3</sub> CD <sub>2</sub> OH	0	0.08	0	0.55	0.60
CD <sub>3</sub> CD <sub>2</sub> OH	0	0.00	0	1.00	--
CH <sub>3</sub> CD <sub>2</sub> OH	0	0.05	0	0.62	0.57
CD <sub>3</sub> CH <sub>2</sub> OH	0	0.07	0	0.69	0.65
CH <sub>3</sub> CH <sub>2</sub> OH	0.204	0.04	0.191	0.33	
CH <sub>3</sub> CH <sub>2</sub> OH	0.198	0.03	0.198	0.25	
CD <sub>3</sub> CD <sub>2</sub> OD	0.193	0.01	0.204	0.26	
CH <sub>3</sub> CH <sub>2</sub> OD	0.192	0.03	0.194	0.29	
CD <sub>3</sub> CD <sub>2</sub> OH	0.208	0.01	0.194	0.33	
CH <sub>3</sub> CD <sub>2</sub> OH	0.209	0.03	0.199	0.35	
CD <sub>3</sub> CH <sub>2</sub> OH	0.188	0.03	0.189	0.45	



liquid phase runs.

iv) -112°C Gas Fraction

This gas fraction was analysed from mass spectrometric cracking patterns (at electron bombardment of 76 e.v.) for the light ethanol samples only. These analyses are contained in Table III-32. Lack of proper standards for mass spectrometer calibration and overlap of the cracking patterns of the products precluded this type of analysis for the deuterated alcohol -112°C gas fractions. Nevertheless, significant facts could be gleaned from examination of low voltage ( $\approx 10$ -15 e.v. electron energy) mass spectrograms run on these samples. To insure the absence of any contribution to the ethylene m/e peaks from ethane "the low voltage scans" were run at an electron energy below the appearance potential of ethane ions. Table III-33 contains ratios of some ethylene and acetylenes from the radiolysis of deuterated ethanols. These ratios assume that the sensitivities of various isotopic forms of the same compound are the same.

b) Liquid Products.

i) Acetaldehyde

Acetaldehyde yields could only be obtained from  $C_2H_5OH$  and  $C_2H_5OD$ . The rest of the alcohols contained sufficient amounts of acetal as an impurity to render acetal analysis futile (see Table II-1). Blank samples could not be used to subtract a correction from the observed results because the amount of acetal present in each sample would be



-112°C GAS FRACTION PRODUCT YIELDS FROM LIGHT ETHANOL CONTROL RUNS FOR DEUTERATED SAMPLES.

Type of Sample	$\zeta_p$	Dose (e.v./cc.)	$G(C_2H_6)$	$G(C_2H_4)$	$G(C_2H_2)$	$G(C_3H_8)$
liquid	0	$2.82 \times 10^{20}$	0.22	0.11	0.016	0.012
liquid	0	$2.84 \times 10^{20}$	0.19	0.14	0.002	0.013
liquid	0.204	$2.79 \times 10^{20}$	0.05	0.08	0.03	0.005
liquid	0.198	$2.80 \times 10^{20}$	0.04	0.10	0.01	0.005
gas	0	$3.32 \times 10^{20}$	0.19	1.15	0.10	0.012
gas	0	$3.32 \times 10^{20}$	0.20	1.14	0.08	0.009
gas	0.191	$3.17 \times 10^{20}$	0.01	0.87	0.26	0.009
gas	0.198	$3.15 \times 10^{20}$	0.02	0.88	0.30	0.008





TABLE III-33

RATIOS OF SOME ETHYLENES AND ACETYLENES FROM THE  
RADIOLYSIS OF DEUTERATED ETHANOLS.

Alcohol		Pure Liquid	Pure Gas	Inhibited Liquid	Inhibited Gas
CD <sub>3</sub> CD <sub>2</sub> OD	$\frac{C_2D_4}{C_2D_3H}$	26	45	--	38
	$\frac{C_2D_2}{C_2H_2}$	--	--	--	2.0
CH <sub>3</sub> CH <sub>2</sub> OD	$\frac{C_2H_4}{C_2H_3D}$	9.6	7.8	20.3	11.7
	$\frac{C_2H_2}{C_2HD}$	--	11.3	--	20.9
CD <sub>3</sub> CD <sub>2</sub> OH	$\frac{C_2D_4}{C_2D_3H}$	20.6 <sup>1)</sup> 23.0 <sup>2)</sup>	6.9 <sup>1)</sup> 5.6 <sup>2)</sup>	28	10.9
	$\frac{C_2D_2}{C_2HD}$	--	>25	>5	28
	$\frac{C_2D_2}{C_2H_2}$	--	--	1.0	2.0
CH <sub>3</sub> CD <sub>2</sub> OH	$\frac{CH_2CD_2}{CH_2CDH}$	5.7	2.6	>26	2.5
	$\frac{C_2D_2}{C_2HD}$	1.0	1.0	--	1.3
	$\frac{C_2D_2}{C_2H_2}$	--	6.0	--	0.6
CD <sub>3</sub> CH <sub>2</sub> OH	$\frac{CD_2CH_2}{CD_2CHD}$	>29	2.1	>15	1.8
	$\frac{CD_2CH_2}{CHDCH_2}$	--	27	--	13.5
	$\frac{C_2D_2}{C_2HD}$	--	1.5	--	1.5
	$\frac{C_2D_2}{C_2H_2}$	--	--	--	1.0



increasingly greater in each successive sample prepared (boiling point of acetal =  $102-104^{\circ}\text{C}$ ; boiling point of ethanol =  $78^{\circ}\text{C}$ ). In fact,  $\text{C}_2\text{H}_5\text{OD}$  also contained some acetal. However, as the analysed samples were prepared from a relatively large amount of alcohol in the reservoir ( $\approx 30$  ml.) the composition of the samples was more constant than for the other alcohols. This fact, combined with the analysis of two blank samples (one prepared before and one after the radiolysed samples) renders the aldehyde yields from this alcohol credible.  $G(\text{acetaldehyde})$ , (actually  $G(\text{acetaldehyde} + \text{acetal})$ ) values are outlined in Table III-34.

ii) 2,3-Butanediol

Analysis for this product gave detectable amounts of 2,3-butanediol for  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OD}$  and  $\text{C}_2\text{D}_5\text{OD}$  only. This disturbing fact can be reconciled to the fact that the three alcohols that showed no glycol in both liquid and gas phase samples all had an impurity in common. The three above mentioned alcohols that exhibited measurable glycol yields did not contain this impurity. It has been demonstrated (see Figure III-14(B)) that very small amounts of some compounds can greatly inhibit the production of 2,3-butanediol. Precautions outlined in the Experimental Section rule out the possibility that traces of 1,3-pentadiene left in the system from earlier sample preparation caused diminution of the 2,3-butanediol.

Table III-34 shows the 2,3-butanediol yields that could be measured.





TABLE III-34

LIQUID PRODUCT YIELDS FROM SOME ETHANOL AND ETHANOL -1,3-PENTADIENE MIXTURES (LIGHT AND DEUTERATED ETHANOLS).

Alcohol	Sample	G(Acetalde- hyde)	G(1,2-Propane- diol)	G(2,3-But- anediol)
CH <sub>3</sub> CH <sub>2</sub> OH	pure liquid	1.84	0.12	2.32
	pure liquid	1.81	0.12	2.54
	inhibited liquid	1.46	--	--
	inhibited liquid	1.50	--	--
	pure gas	3.30	0.80	3.36
	pure gas	3.67	0.92	2.89
	inhibited gas	1.28	--	--
	inhibited gas	1.50	--	--
CH <sub>3</sub> CH <sub>2</sub> OD	pure liquid	3.34	--	2.04
	inhibited liquid	1.31	--	--
	pure gas	2.14	0.55	3.19
	inhibited gas	1.31	--	--
CD <sub>3</sub> CD <sub>2</sub> OD	pure liquid	--	--	1.70
	pure gas	--	0.80	2.33



iii) 1,2-Propanediol

This product could be measured in the gas phase samples in which the C<sub>4</sub> glycol could also be measured and also in the light ethanol liquid samples. Table III-34 includes these numbers.



## DISCUSSION

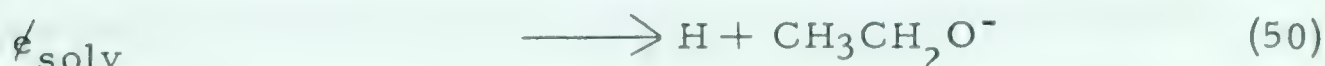
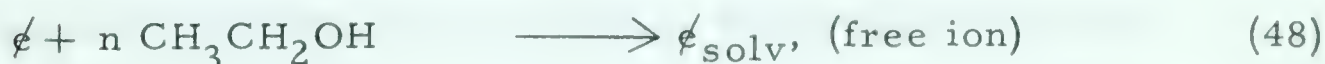
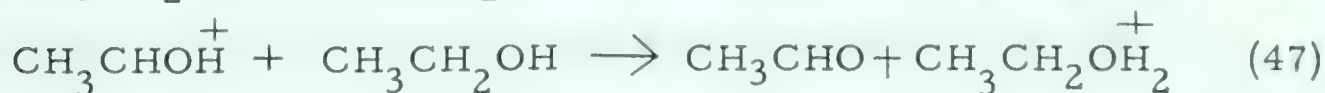
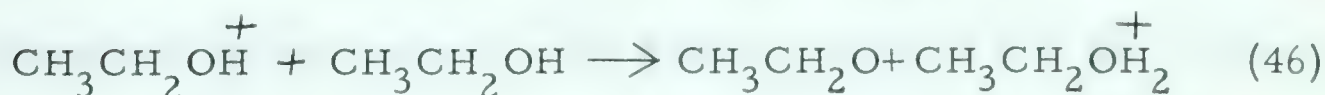
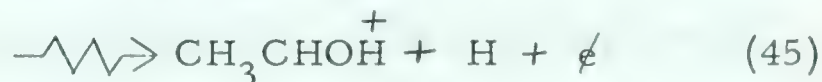
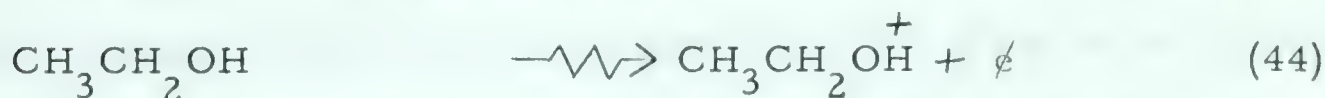
### (A) Liquid Ethanol Radiolysis

#### a) Main Products

As hydrogen, acetaldehyde and 2,3-butanediol are the main products, they will be discussed first. These products accounted for more than 85% of the total observed product yield at doses  $< 1 \times 10^{20}$  e.v./gm. Several possible mechanisms for their production were considered and a mechanism that incorporated many of the features of one proposed by Baxendale and Mellows<sup>(58)</sup> for methanol radiolysis was found to explain the observed results. The main features of the overall reaction are as follows:

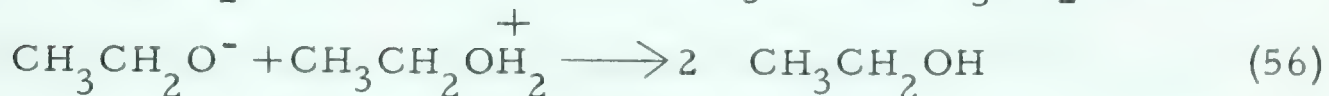
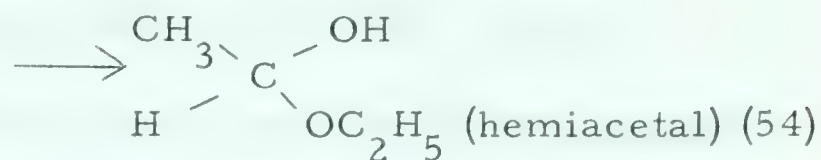
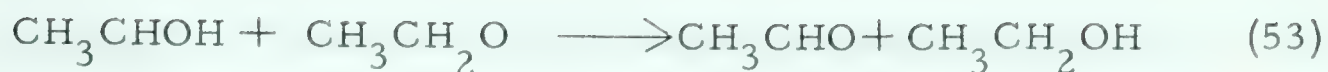


The reaction mechanism probably includes the following steps:



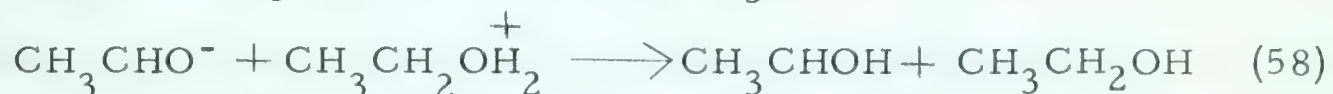






The hemiacetal formed in reaction (54) is equivalent to an acetaldehyde molecule in the analytical system used in the present work.

At doses from  $10^{18}$  e. v. /gm. to  $10^{20}$  e. v. /gm. and greater, reactions (57) and (58) become important.



Reactions (44) - (58) account for a large part of the observed hydrogen, acetaldehyde and 2, 3-butanediol.

The mechanism does not involve excited molecules as such. However the reaction (45) is simply reaction (44) involving a more energetic precursor. The electron in reaction (49) does not get away from the spur as does the electron in reaction (50). Reaction (49) would occur if reaction (46) occurred. The results indicate that reactions (44) and (45) occur in the liquid phase to comparable extents.

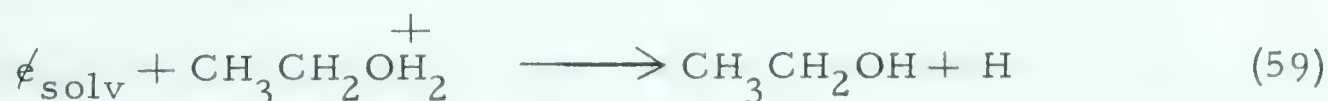
In a recent mass spectrometric study of ion-molecule reactions, Ryan et al<sup>(102)</sup> found that  $\text{CH}_3\text{CHOH}^+$  is an important precursor for the formation of  $\text{CH}_3\text{CH}_2\text{OH}_2^+$  by reaction (47) in such systems.



Hydrogen . Various workers have reported that the value of  $G(H_2)$  decreases with increasing dose<sup>(23), (30), (103)</sup>. In the ethanol system both electrons and hydrogen atoms have been suggested as being precursors of hydrogen<sup>(103)</sup>. (The same precursors had been considered previously in the methanol system<sup>(25), (44)</sup>.) The evidence indicates that the electron precursor is more sensitive to impurities than is the hydrogen atom.

The decrease in  $G(H_2)$  from 4.9 to 4.2 when the dose increases from  $1 \times 10^{18}$  to  $1 \times 10^{20}$  e.v./gm. can be explained by reactions (57) and (58). Adams and Sedgwick<sup>(103)</sup> found that acetaldehyde is a more efficient electron scavenger than are chloroacetic acid and carbon tetrachloride (two substances that have been used to trap electrons in radiolytic systems)<sup>(43), (104), (105)</sup>.

An alternative to reaction (57) as a fate for the solvated electron is



The electron in this reaction is not the same as the electron in reaction (49) which does not escape from the spurs.

Adams and Sedgwick have suggested that reaction (59), in the bulk medium, is unimportant in neutral ethanol. This can be demonstrated through kinetic considerations. The pK for auto-ionization of pure ethanol is 19.1<sup>(106)</sup>. Therefore, the concentration of  $\text{CH}_3\text{CH}_2\text{OH}_2^+$  in pure ethanol is  $3 \times 10^{-10}$  moles per liter. The value of  $G(e_{\text{solv}})$  is approximately 1. The rate of production of





$\text{CH}_3\text{CH}_2\text{OH}_2^+$  from radiolysis at a dose rate of  $5 \times 10^{18}$  e.v./gm-hour is calculated to be  $2 \times 10^{-11}$  moles/liter-sec. Taub et al<sup>(48)</sup> have measured the rate constant for the reaction of solvated electrons with protons in ethanol (presumably present as  $\text{CH}_3\text{CH}_2\text{OH}_2^+$ ) and found a value of  $k = 2.0 \times 10^{10}$  liters moles<sup>-1</sup> sec<sup>-1</sup>. \* Hence the steady state concentration of  $\text{CH}_3\text{CH}_2\text{OH}_2^+$  from the radiolysis would be  $3 \times 10^{-11}$  moles per liter if there were no auto-ionization. This is an order of magnitude less than that which actually exists due to auto-ionization. So it appears that most solvated electrons would react with ions from auto-dissociation, if reaction (59) were important.

The rate constant for  $\text{C}_2\text{H}_5\text{OH}_2^+ + e_{\text{solv}}$  is 12.5 times that for  $\text{CH}_3\text{CHO} + e_{\text{solv}}$ <sup>(103)</sup>. Thus the value of the rate constant for  $e_{\text{solvated}} + \text{CH}_3\text{CHO}$  is  $1.6 \times 10^9$  liters mole<sup>-1</sup> sec<sup>-1</sup>.

Using these rate constants, it was found that the reactions of solvated electrons with  $\text{CH}_3\text{CH}_2\text{OH}_2^+$  and with acetaldehyde would progress at equal rates when the aldehyde was present at a concentration of  $4 \times 10^{-9}$  moles per liter. Since  $G(\text{acetaldehyde}) \approx 2$ , this concentration would be reached at a dose of about  $1 \times 10^{14}$  e.v./ml., or about five orders of magnitude too low to account for an electron scavenging effect of acetaldehyde, if it were competing against reaction (59).

---

\* A value of  $4 \times 10^{10}$  liters moles<sup>-1</sup> sec<sup>-1</sup> can be calculated from the Smoluchowski equation<sup>(107)</sup>.



The half way point for the decrease from  $G(H_2) = 4.9$  to 4.2 is at  $1 \times 10^{19}$  e.v./gm. At this dose the concentration of acetaldehyde is  $2.6 \times 10^{-4}$  moles/liter. If the rates of the reaction of the solvated electron with acetaldehyde (reaction 57) and the first order decomposition of the solvated electrons (reaction 50) were equal at a dose of  $1 \times 10^{19}$  e.v./gm., then

$$\begin{aligned} k_{50} &= k_{57} \times [CH_3CHO] \text{ at } 1 \times 10^{19} \text{ e.v./gm.} \\ &= 1.6 \times 10^9 \text{ liters moles}^{-1} \text{ sec}^{-1} \times 2.6 \times 10^{-4} \frac{\text{moles}}{\text{liter}} \\ &= 4.2 \times 10^5 \text{ sec}^{-1} \end{aligned}$$

Therefore the half life of the solvated electron would be

$$\frac{.69}{4.2 \times 10^5} \approx 2 \times 10^{-6} \text{ sec.} \approx 2 \mu \text{ sec.}$$

Taub et al<sup>(63)</sup> have measured the half life of the solvated electron in ethanol and found  $\tau = 3 \mu \text{ sec.}$  They suggest that the decay of the solvated electron concentration is due to combination of the electrons with ethanol ions, although they do not dismiss other possibilities. Because of the close agreement between their half life and the above value calculated from competitive kinetics, it appears very likely that the decay of the electron is due to reaction (50).

Thus there is strong evidence that the decrease in  $G(H_2)$  from 4.9 to 4.2 is due to scavenging of solvated electrons by acetaldehyde. This value of  $G(\phi_{\text{solv}}) = 0.7$  falls within the error limit of the estimation of  $1.0 \pm 0.3$  by Taub et al<sup>(63)</sup>. Adams and





Sedgwick<sup>(103)</sup> report a value of 1.0 which includes a contribution of  $G = 0.07$  for the following reaction



Addition of this figure to the present value would result in  $G(\text{solvated electrons}) = 0.8$ .

The foregoing considerations make it evident that to obtain initial yields which are unaffected by secondary reactions it is important to use very pure ethanol and to irradiate to low doses. Impurities that scavenge electrons would inhibit reaction (50) and thereby reduce the hydrogen yield.

It is significant that the present  $G_i(\text{H}_2) = 4.9$  agrees with values from two other  $\gamma$  - radiolysis liquid studies<sup>(43), (103)</sup> that were carried out in low dose ranges. Lower values that have been reported have been invariably obtained at high doses ( $> 1 \times 10^{20}$  e. v. /gm.).

From the foregoing comments, it might be thought that the degree of purity of the ethanol that is radiolized can be judged by how high a value of  $G_i(\text{H}_2)$  is reported. This is not the case. It has been demonstrated<sup>(103)</sup> that the addition of small amounts of acid results in higher  $G(\text{H}_2)$  values than those observed in neutral ethanol. Thus, high  $G_i(\text{H}_2)$  values do not necessarily indicate that pure ethanol was radiolized. The method of purification of the ethanol must be one that does not leave any traces of acid in the alcohol.





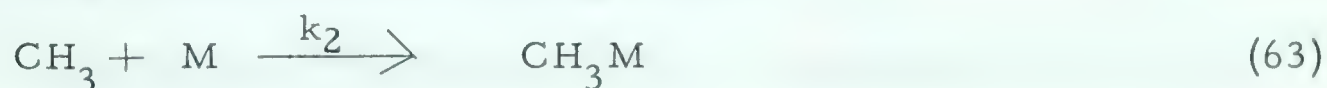
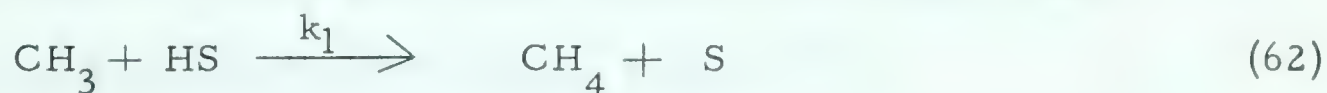
It should be noted that all inhibition experiments were carried out at high doses (to give measureable concentrations of liquid products) and so the yield of hydrogen was about  $G = 4.2$ . That is, reaction (57) was proceeding to the exclusion of reaction (50).

Although both benzene and 1,3-pentadiene (hereafter synonymous with "diene") reduced  $G(H_2)$  the effect of the latter was the more pronounced. The hydrogen atom scavenging reaction of benzene



has been considered previously<sup>(9), (3), (103)</sup>. However, Szwarc et al<sup>(109), (110)</sup> have studied the methyl affinities of various hydro-

carbons by determining the relative rates of the following reactions



where HS is a hydrocarbon solvent and M is the compound whose methyl scavenging power is to be measured. When M was 1,3-pentadiene they found  $k_2/k_1 \approx 1000$ ; when M was benzene  $k_2/k_1 \approx 0.3$ . It therefore appears that the radical scavenging ability of benzene is such that, at best, it is a weak radical trap compared to the diene.

It has been suggested that small amounts of benzene present in a liquid hydrocarbon radiolytic system act predominantly through "physical interactions", i.e. excitation and/or charge transfer<sup>(111)</sup>.

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An energy transfer mechanism of the type



(where  $\text{X}^*$  is a precursor of hydrogen) is feasible. However, excited molecules appear to play a small role in the radiolysis. If they are important, they appear to result in essentially the same product distribution as do the ions.

As benzene has a negative electron affinity<sup>(112)</sup> its action does not involve direct electron scavenging. Benzene would not interfere with the proton transfer reaction (47) by accepting the proton, since its gas phase proton affinity is 144 kcal/mole compared to 185-202 kcal/mole for ethanol<sup>(35)</sup>.

The ionization potentials<sup>(113)</sup> of 1,3-pentadiene (9.0 e.v.) and benzene (9.3 e.v.) are both lower than that of ethanol (10.5 e.v.). (The value for the diene was estimated from data for 1-butene, 1,3-butadiene and 1-pentene.) Therefore, processes such as



(where P is benzene or 1,3-pentadiene) are possible. This would inhibit reaction (46) and cause a decrease in  $G(\text{H}_2)$ .

The 1,3-pentadiene has been shown to be an efficient radical scavenger<sup>(109)</sup>. ESR studies have shown that if the hydrogen atom is generated as such, it has a short lifetime in the ethanol system due to its reactivity. The question as to how efficient





the diene is, as a hydrogen atom scavenger, in the present system is therefore largely speculative. However, the diene is certainly a better protector than is benzene. In view of its greater ability to scavenge radicals<sup>(109), (110)</sup>, the larger decrease in  $G(H_2)$  per unit concentration compared to benzene is probably due to hydrogen atom scavenging. The possible role of 1,3-pentadiene as a charge transfer agent is, however, not to be ignored. It is in accord with the observed data that benzene acts as a charge transfer agent (plus a weak radical scavenger) while the diene traps radicals efficiently and contributes some protection through charge transfer. That is, both benzene and 1,3-pentadiene reduce  $G(H_2)$  by interfering with the same processes at different stages.

The fact that benzene does not act only as a radical trap can be seen from the 2,3-butanediol results. The pentadiene is about 100 times as efficient in reducing the glycol yield, while it is a better radical trap by a factor of  $3 \times 10^3$ . Therefore, benzene must act by a second mode (charge transfer).

Table IV-1 contains excitation energies and ionization potentials for ethanol and the two inhibitors. If excited ethanol molecules take part in these reactions, benzene and 1,3-pentadiene could also act in energy transfer reactions.

Considering the  $G(H_2)$  vs.  $\epsilon_p$  plot of Figure III-11 (B), the gently decreasing portion of the curve from  $\epsilon_p = 0.1$  to 1.0 can be roughly extrapolated back to  $\epsilon_p = 0$  at a  $G(H_2)$  value of



TABLE IV-1

Lowest Singlet and Triplet Excitation Energies and Ionization  
Potentials

The units are e. v.

<u>Compound</u>	<u>Triplet</u>	<u>Singlet</u>	<u>I. P.</u>
$C_2H_5OH$	—	$\sim 6.9$ b	10.48 a
$C_6H_6$	3.59 b	4.76 b	9.25 a
1,3 - $C_5H_8$	2.6 c	5.4 c	9.0 d

- a) Reference (113)
- b) Reference (114)
- c) Reference (115)
- d) Obtained by comparing the I. P. 's of 1-butene, 1,3-butadiene and 1-pentene from reference (113).



$G \approx 1.5$ . This would represent the hydrogen that is largely unaffected by diene scavenging and will be termed "unscavengeable hydrogen". The difference between  $G(\text{H}_2) = 4.2$  and  $G = 1.5$ , following the scheme of Adams and Sedgwick<sup>(103)</sup>, would correspond to  $G(\text{H atoms}) = 2.7$ . The values,  $G(\text{solvated electrons}) \approx 0.8$ ,  $G(\text{H}) \approx 2.7$ , and  $G(\text{H}_2) \text{ unscavengeable} \approx 1.5$  found in the present investigation are in rough agreement with the previously reported values<sup>(103)</sup>:  $G(\text{solvated electrons}) = 1.0$ ,  $G(\text{H atoms}) = 2.3$ , and  $G(\text{H}_2) \text{ unscavengeable} = 1.7$ .

The source of the unscavengeable hydrogen is uncertain but is possibly a combination of molecular hydrogen, i.e.



and hydrogen atoms from reactions (45) and (49) that have excess energy ("hot hydrogen atoms").

### 2,3-Butanediol and Acetaldehyde

Although reactions such as



cannot be totally disregarded, the most plausible way in which 2,3-butanediol can be formed is by combination of two

$\alpha$ -ethanol radicals



The high yield of 2,3-butanediol ( $G = 2.2$ ) indicates that  $\text{CH}_3\text{CHOH}$  radicals are a major intermediate in the radiolysis.





Yield data for this product from other liquid room temperature studies show poor agreement. G values of 1.00, 1.27, 1.40, 1.67, 1.95, and 2.80 are given in references (17) (47) (30) (43) (23) and (103) respectively. The large scatter of the results may reflect upon the presence of impurities or difference in analytical techniques. Most values were obtained by periodic acid reduction equivalence<sup>(116)</sup>. The present data were obtained by gas chromatography and the 2,3-butanediol yield exhibited little or no dependence on dose over the region studied. As the 2,3-butanediol that was used for calibration solutions was checked for purity by gas chromatography, the present results are deemed to be trustworthy.

Physical evidence (E. S. R. measurements) for the presence of  $\text{CH}_3\text{CHOH}$  in ethanol systems has been presented in the Introduction Section. The presence of hydrogen atoms in irradiated ethanol systems has not been established by such studies. This may indicate that they react too quickly (abstracting from a substrate molecule), even at low temperatures, to be detected.

The  $\alpha$ -ethanol radicals arise in the system by reaction (51) of the mechanism. The suggestion that hydrogen atom abstraction occurs mostly from the methylene group is supported by bond strength considerations (see page 16) and results obtained from aqueous solutions of deuterated ethanols<sup>(66)</sup>.



To fit the observed results (including those from inhibitor studies), it is necessary to assume a small value for the disproportionation to combination ratio for  $\alpha$ -ethanol radicals. Such a situation has been suggested in a Hg photosensitized study of ethanol vapor<sup>(79)</sup>, (ratio = 0.3), although an even smaller ratio ( $< 0.1$ ) is necessary in the radiolytic system to account for the present data. This premise that  $\alpha$ -ethanol radicals dimerize only, is fortified by a statement of Knight and Gunning in a study of Hg photosensitized methanol that "it appears unlikely that  $\text{CH}_2\text{OH}$  radicals are involved in formaldehyde formation"<sup>(77)</sup>.

The analytical system was capable of measuring the relative amounts of meso and d,l - 2,3-butanediol at high doses. In samples irradiated to a dose of  $> 9 \times 10^{20}$  e.v./gm. a doublet gas chromatographic peak, due to the two geometric forms of the glycol, was evident. At this dose the meso and d,l forms were produced in approximately equal quantities.

The inhibitory effect upon this product was much more pronounced with the diene than with benzene. The results strongly indicate that the glycol is formed in the bulk medium by a mechanism which involves scavengeable entities. Again, the observed difference in behaviour of the two protectors, makes it plausible that they may be interfering with the same process at different concentrations of additive. From the considerations outlined above, it is reasonable that benzene reduces the





glycol yield largely by a charge transfer mechanism, while the di-olefin mechanism involves charge transfer to some extent but the pentadiene also has the ability to effectively scavenge any  $\text{CH}_3\text{CHOH}$  radicals that arise in the bulk medium.

$G_i(\text{acetaldehyde}) = 1.9$ . Previous liquid phase

$\gamma$ -radiolysis investigators have cited the following  $G(\text{acetaldehyde})$  values: 1.40, 1.88 and 3.14 (references (23) (47) and (43) respectively). The low value of 1.40 is suspect<sup>(23)</sup>, because in that study  $G(\text{acetaldehyde} + 2,3\text{-butanediol}) = 3.35$ , which should closely approximate  $G(\text{H}_2) = 5.5$  at the prevailing dose ( $2 \times 10^{20}$  e.v./gm.).

The overall mechanism has two different paths by which acetaldehyde may be formed. The first is the proton transfer reaction (47) which should not be affected by inhibitors. The second involves radical-radical reactions of ethoxy radicals (reactions 53-55). At high doses acetaldehyde is destroyed by reaction (57) followed by (58). The encounter of two ethoxy radicals is assumed to result mainly in disproportionation, in contrast to the case of  $\alpha$ -ethanol radicals. The intermediate case of  $\alpha$ -ethanol radical plus ethoxy radical may give both disproportionation and combination. However, as mentioned previously, both products (acetaldehyde and hemiacetal) would be equivalent in the present analytical system.



At the doses employed for acetaldehyde determination part of the acetaldehyde would be lost by reaction (57) prevailing over reaction (50).

Therefore, it is significant that Hayon and Weiss<sup>(43)</sup> found a high value for G acetaldehyde (= 3.1) at low doses ( $\approx 1 \times 10^{16}$  e.v./gm.) where the unimolecular decomposition of the solvated electron would not be interfered with by the electron scavenging mechanism involving acetaldehyde (reactions (57) and (58)). It, therefore, appears that the decrease in  $G(H_2)$  with increasing dose is accompanied by a concomitant decrease in acetaldehyde, as the electron scavenging mechanism would require. Unfortunately, the present analytical system did not allow accurate measurements of the liquid products at low doses ( $< 1 \times 10^{20}$  e.v./gm.). Nevertheless, the mechanism cited above is consistent with the data for the radiolysis of ethanol at doses less than  $1 \times 10^{20}$  e.v./gm.

Neither benzene nor 1,3-pentadiene had an appreciable effect on the acetaldehyde yield over the whole concentration range of the two additives. The most conclusive and reliable data come from the pentadiene-ethanol studies where  $G(\text{acetaldehyde})$  could be measured over the whole concentration range. To explain lack of inhibition of acetaldehyde by diene, it must be postulated that either (i) diene reacts with free  $e_{\text{solv}}$ , thereby inhibiting reaction (57) or (ii) if diene does not react with  $e_{\text{solv}}$ , reactions





(53-55) must occur mainly in the spurs. It appears that (i) is more likely, because reaction (52) occurs in the bulk medium and is readily inhibitable by the diene.

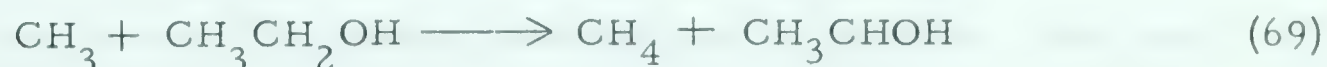
## b) Minor Products

Although the three products previously discussed (hydrogen, 2,3-butanediol and acetaldehyde) account for the major part of the radiolysis reaction, some 15% of the observed products arise from alternative routes. Therefore each product, its yield, and likely modes of formation will be discussed below to complete the radiolysis mechanism. More liberal use of excited molecule precursors can satisfy the observed results for these products compared to those discussed above.

### Methane

This product had a G value of 0.6. The yield values in the literature for methane range from  $G = 0.4$  to  $G = 0.8$ <sup>(23)(30)(43)(44)</sup>. Within experimental error, references (43) and (44) give the same yield as that found in the present work.

One possible mode of formation for methane is the following:

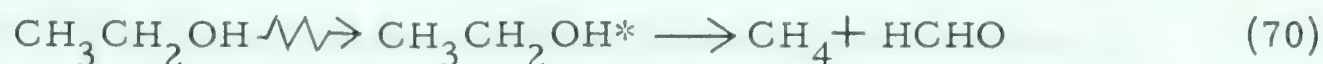


Again, the methylene group of the ethanol molecule is the most probable site of attack for the reasons outlined previously,



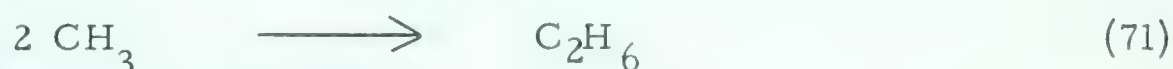


A second mechanism for methane formation could be by a molecular reaction, i.e.



If this were the predominant mode of methane formation, the yields of methane and formaldehyde would be nearly equal. However, the methane yield was 4-5 times that of formaldehyde. Even if all the carbon monoxide found was assumed to arise from formaldehyde decomposition, the combined yields of carbon monoxide and formaldehyde would still only account for one third of the methane. Therefore, it appears that reaction (70) is not the chief path of methane production.

If it is assumed that each chemically observable C - C bond break eventually gives rise to a molecule of methane, i.e. if radical-radical reactions such as



are neglected, the ratio of  $\frac{G(\text{CH}_4)}{G(\text{H}_2)}$  would reflect the ratio of primary C - C breakages/C - H + O - H breakages. The ratio is 0.12. If this figure is multiplied by 6 (the ratio of bonds to hydrogen to C - C bonds in the molecule) the result is 0.7. Thus, it appears that despite the fact that the C - C bond is the weakest in the molecule, C - H or O - H scission predominates. However, the cage effect may mask a large part of the C - C bond rupture.

Methane exhibited the same sort of behaviour as hydrogen with additives (in the high dose region). That is, the diene reduced



$G(\text{CH}_4)$  more quickly than did benzene and the  $G(\text{CH}_4)$  vs.  $\epsilon_p$  plot could be interpreted by assuming a scavengeable radical precursor ( $\text{CH}_3$ ) for part of the methane and a non-scavengeable precursor for the balance. Using the  $\epsilon_p$  vs.  $G(\text{CH}_4)$  plot of Figure III-12(B), extrapolation of the gradually decreasing portion of the curve to  $\epsilon_p = 0$  gives a value of  $G(\text{CH}_4) \approx 0.15$ . Therefore, about three quarters of the methane has a methyl radical precursor while one quarter is unscavengeable due to a process of the type



or spur reactions of  $\text{CH}_3$  radicals. The ratio of 3 : 1 scavengeable to unscavengeable methane is in good agreement with that reported in a previous study by Adams, Baxendale and Sedgwick<sup>(44)</sup>:  $G(\text{CH}_4)_{\text{unscavengeable}} = 0.16$ ,  $G(\text{CH}_3) = 0.44$ .

### Carbon Monoxide

This minor product had an initial G value of 0.06 and although the data were scattered, the yield appeared to be constant with dose. Values of 0.05, 0.09, 0.11 and 0.26 (from references (11)(30)(17)(43) respectively) have been reported. To form carbon monoxide by a one-step molecular process of the type

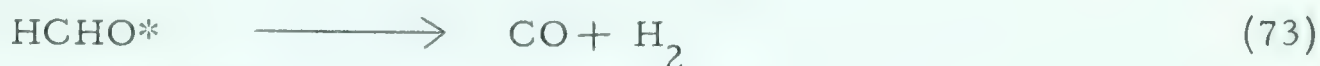


four bonds would have to be split simultaneously. Therefore, it appears that this process is very unlikely and that the immediate precursor of carbon monoxide must be a reactive intermediate

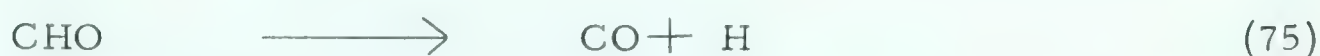
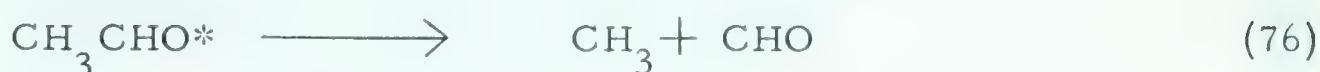




formed from the decomposition of the ethanol. Likely species would be excited formaldehyde and acetaldehyde. Thus formaldehyde could give rise to carbon monoxide by



Similarly,



Carbon monoxide, like acetaldehyde, was not affected by 1,3-pentadiene. (Its behaviour with added benzene could not be determined accurately.) If the immediate precursor to the monoxide is radical in nature, it must be highly energetic or the reaction must proceed in the spurs.

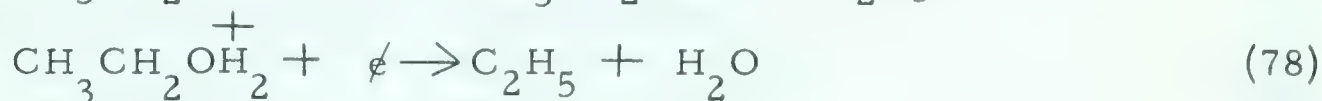
### Ethane and Ethylene

$G_1(\text{ethane}) = 0.24$  and the yield showed no dose dependence. Previously reported values range from 0.17 to 0.30<sup>(17)(30)(103)(23)</sup>.

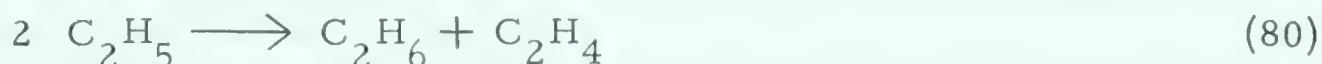
$G_1(\text{ethylene})$  was approximately 0.14. Literature values range from 0.1 to 0.27<sup>(103)(17)(30)(23)</sup>. In the present study the ethylene yield was found to decrease with dose. The amount of ethylene at a given total dose increased with dose rate, which probably indicates that the dose dependence of the yield decreases with increasing dose rate.



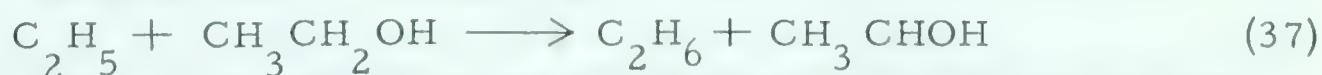
With respect to the mechanism of ethane formation, the only reasonable precursor for its generation is the ethyl radical. Physical evidence for the presence of the ethyl radical in ethanol photolysed in the solid state has been obtained in an E.S.R. study by Sullivan and Koski<sup>(68)</sup>. In liquid radiolytic systems, a number of feasible processes can give rise to ethyl radicals



Lapporte<sup>(118)</sup> and Cvetanovic<sup>(119)</sup> cite ratios of 0.12 and 0.11 for the ratio of disproportionation to combination of ethyl radicals in the gas phase. The yield of butane from the radiolysis was  $G = 5 \times 10^{-4}$ . Therefore, if the same disproportionation to combination rates applies in the present system, the yields of ethane and ethylene from



are negligible. If the ethyl radicals do not produce significant quantities of ethane by reaction (80), the most logical process for ethane formation is an abstractive step.



Ethane would also be a product of processes such as



where R is another radical.



A molecular process for the generation of ethylene, analagous to that cited in pyrolysis mechanisms<sup>(120), (121)</sup>



is easily envisaged; although Barnard and Hughes<sup>(121)</sup> claim that reaction (82) is not important under their pyrolysis conditions. As the concentration of ethylene in the system increases, the probability for the reaction



increases. This fact probably accounts for the observed decrease in G(ethylene) at progressively higher doses.

As the ethyl radical is the entity that gives rise to ethane, it is not surprising that both benzene and diene inhibit this product. Treating the pentadiene plot as was done for the analagous hydrogen and methane graphs, it is seen that approximately two thirds of the ethane is easily scavenged, while one third is little affected by the presence of the inhibitor. This one third is probably the result of spur reactions of ethyl radicals while the inhibition is due to radicals that are trapped in the bulk medium.

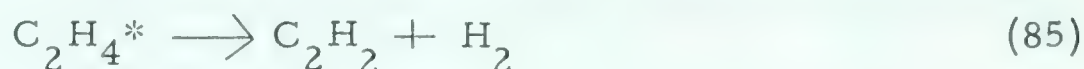
Benzene and 1,3-pentadiene did not reduce the ethylene yield. In fact, it appeared that small amounts of pentadiene actually increases G(ethylene) from that observed in pure ethanol at the dose employed. An explanation for this fact is that pentadiene removes radicals that would otherwise react with ethylene to give other products by reaction (83).



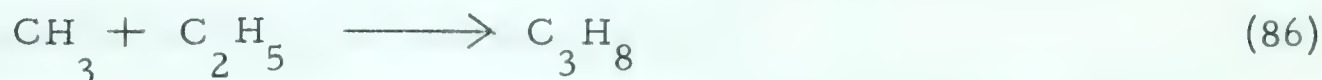


### Acetylene, Propane and Butane

These minor hydrocarbon products can hardly result from primary decomposition of ethanol. A reasonable process for the production of acetylene, ( $G \approx 0.02$ ), would probably involve ethylene as an immediate precursor:



The presence of propane in the system can be most conveniently explained by a reaction between methyl and ethyl radicals



The yield of propane is small, ( $G = 0.009$ ), and since its formation depends upon the encounter of two free radicals, the most favourable conditions for its generation would be found in spurs. This suggestion is supported by the fact that 1,3-pentadiene does not affect the propane yield to any appreciable extent.

Butane, ( $G \approx 5 \times 10^{-4}$ ) would arise from the combination of two ethyl radicals.

### Minor Liquid Products

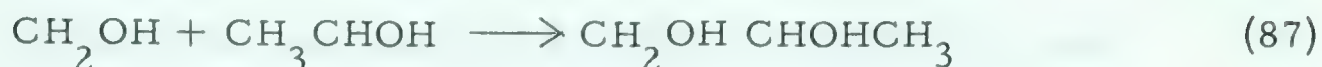
#### Glycols other than 2,3-Butanediol

##### i) 1,2-Propanediol

This diol, which exhibits a G value of 0.13 was the glycol of next highest yield after 2,3-butanediol. It likely arises



from the combination of  $\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CHOH}$  radicals



In analogy with the combination of two  $\alpha$ -radicals it will be assumed that disproportionation reactions are not important. (McDonnell and Newton<sup>(17)</sup> found  $G(\text{methanol}) = 0.06$ ).

The following glycols could only be observed in high dose samples ( $> 3.0 \times 10^{21}$  e. v. /gm.) because of their small yields,

ii) 1, 3-Butanediol

This product had a G value (at  $3.0 \times 10^{21}$  e. v. /gm.)  $\approx 0.05$ .

The most likely reaction for its formation would involve the combination of  $\alpha$ - and  $\beta$ -ethanol radicals.



iii) 1, 4-Butanediol

A G value of  $\approx 0.01$  was found for this glycol. Its formation can be accounted for by the encounter of two  $\beta$ -ethanol radicals



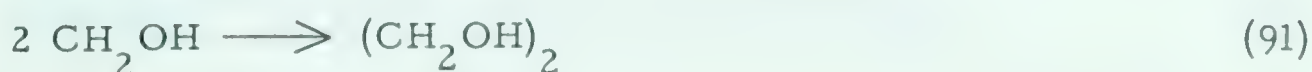
iv) 1, 3-Propanediol

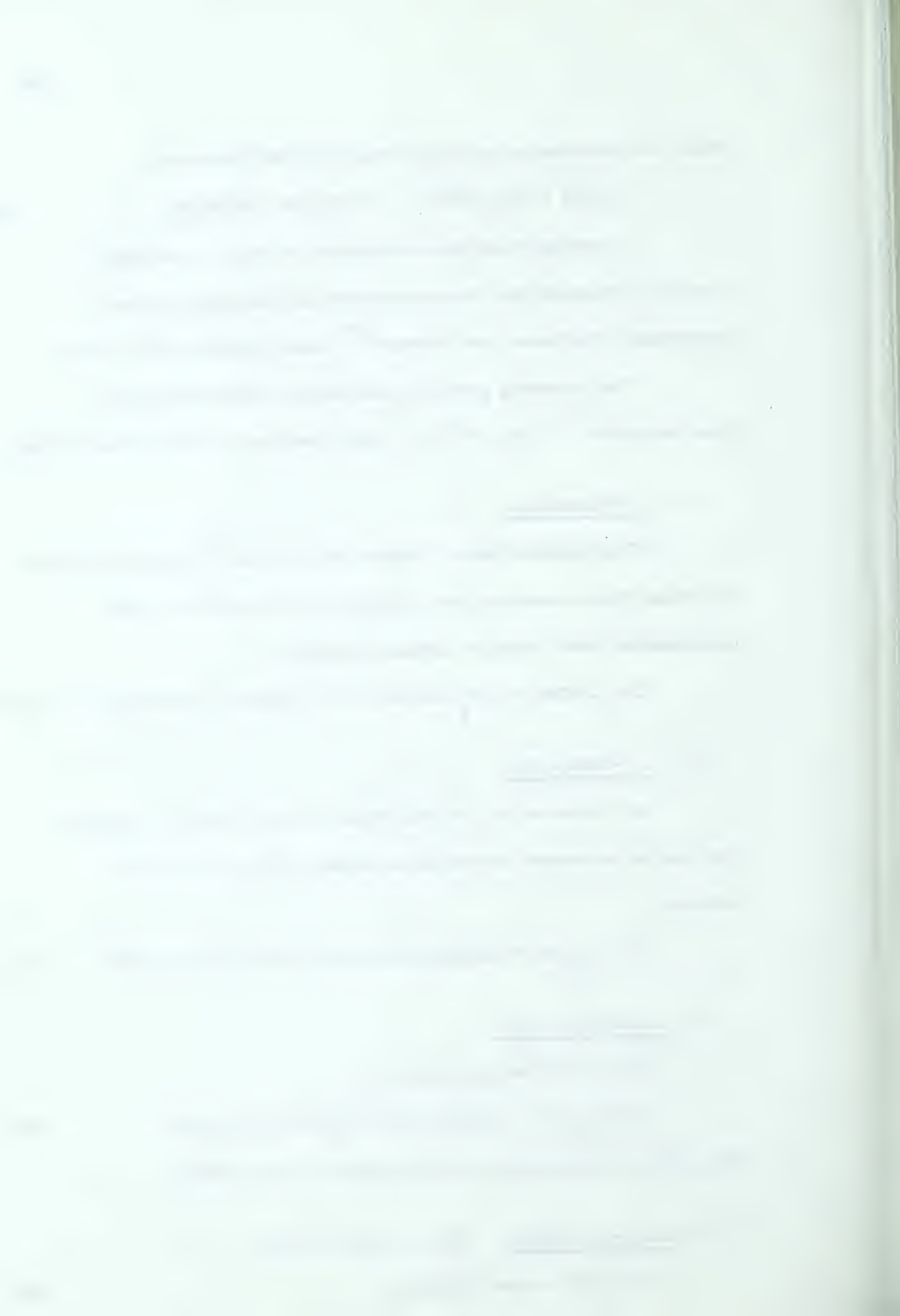
This would be generated by



The yield for this glycol was very small,  $G \approx 0.002$ .

v) Ethylene Glycol. The G value was 0.01.







### Free Radicals and Glycol Formation

The relative amounts of  $\text{CH}_3\text{CHOH}$ ,  $\text{CH}_2\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{OH}$  contained in the glycols (assuming they were produced from the radical-radical reactions outlined above) are presented in Table IV-2. The ratio is 69 : 1 : 4. The figures obtained in the Table were calculated assuming that  $G(2,3\text{-butanediol}) = 2.24$  at the dose where the various other glycols could be measured. The values obtained reflect upon the preferred scission of C - H bonds in the  $\alpha$ -position compared to breakage of C - H bonds in the  $\beta$ -position or of the C - C bond.

The value of the  $\beta$  to  $\alpha$ -ethanol radicals is  $1.5 \times 10^{-2}$ . If it is assumed that this value is due to the difference in energies required to remove a hydrogen atom from the methyl and methylene positions in the ethanol molecule, then the difference would be reflected by

$$10^{-\frac{\Delta E}{RT}} = 1.5 \times 10^{-2} \times \frac{2}{3}$$

where  $\Delta E$  is the difference in activation energies required to account for the relative yields of radicals. The factor  $2/3$  appears due to the fact that there are 3 C - H bonds in the methyl group and 2 for the methylene. From the value of the ratio  $\Delta E \approx 2$  kcals./mole.

### Sec - butyl - alcohol

The presence of sec-butyl-alcohol ( $G = 0.08$ ), among the products is best explained by





TABLE IV-2

Relative Amounts of Radicals that Form Glycol (Liquid  
Ethanol Radiolysis)

Glycol	Amount of radical (CH <sub>3</sub> CHOH)	Amount of radical (CH <sub>2</sub> CH <sub>2</sub> OH)	Amount of CH <sub>2</sub> OH
2, 3 - Butanediol	4.48		
1, 3 - Butanediol	0.05	0.047	
1, 4 - Butanediol		0.024	
1, 2 - Propanediol	0.27		0.27
1, 3 - Propanediol		0.002	0.002
Ethylene glycol	<hr/>	<hr/>	<hr/> 0.020
Total	4.80	0.073	0.292
Ratio	69	:	1
		:	4



### Formaldehyde

This product ( $G = 0.13$ ) would arise from a molecular process



or radical disproportionation



### Water

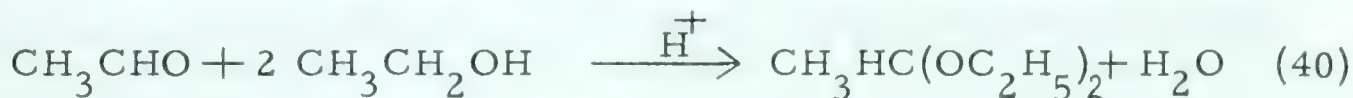
Water can be produced by reaction (82)



or by reactions involving an OH radical that are followed by an abstractive process



The major obstacle to a reliable determination of  $G(\text{H}_2\text{O})$  is a secondary reaction of acetaldehyde which formed acetal and water<sup>(122)</sup>



All previously reported values of  $G(\text{H}_2\text{O})$  had been unaccountably high<sup>(17)(21)(123)</sup>. That is, if one assumes that for each molecule of water formed from direct radiolysis a  $\text{C}_2$  hydrocarbon group (molecule or radical) is also formed, then  $G(\text{H}_2\text{O})$  should be equal to  $G(\text{C}_2\text{H}_6) + G(\text{C}_2\text{H}_4) + G(\text{C}_2\text{H}_2) + G(\text{C}_3\text{H}_8) + 2G(\text{C}_4\text{H}_{10}) + G(\text{sec-butyl-alcohol})$ . This also assumes that a negligible amount of polymer is formed (as was found in previous studies<sup>(17),(21),</sup>)

The total yield of these products is  $G = 0.48$  (assuming  $G(\text{C}_2\text{H}_2) = 0.02$ ) which is in excellent agreement with the observed  $G_i(\text{H}_2\text{O}) = 0.5$ .





The latter figure was obtained by subtracting the water that was formed with the acetal from the total amount measured. The previously reported high values for  $G(H_2O)$  probably resulted from not considering the reaction that formed acetal and water and from faulty analytical technique that did not fully account for the extreme hygroscopic nature of ethanol.

c) Summary

A mass balance for carbon, hydrogen and oxygen, using product yields obtained at a dose of  $2 \times 10^{20}$  e.v./gm., gave an empirical formula of  $C_{2.00}H_{6.11}O_{1.01}$ . This is a reasonable formula when the accuracy with which some of the products were measured is considered.  $G(-Ethanol) = 7.5$ . After correcting for a large unexplained excess of water in a gas phase study of ethanol Ramaradhy and Freeman (21) by a similar treatment found an empirical formula of  $C_{2.00}H_{6.02}O_{0.99}$  and  $G(-Ethanol)$  was 11.1.

A summary of  $G(\text{product})$  values for liquid ethanol radiolysis and the conditions under which they were obtained is given in Table IV-3. There is good agreement between the present work and the latest published data of Adams and Sedgwick(103) who employed approximately the same conditions as were used in the present study.



TABLE IV-3

Comparison of Product Yields from the Radiolysis of Liquid  
Ethanol by Different Workers

Product	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
Hydrogen	3.66	3.46	4.10 <sup>i</sup>	4.87 <sup>i</sup>	4.35 <sup>i</sup>		5.53	4.90 <sup>i</sup>	4.85 <sup>i</sup>
Methane		0.43	0.43 <sup>i</sup>	0.58 <sup>i</sup>	0.60 <sup>i</sup>		0.80	0.6 <sup>i</sup>	0.61 <sup>i</sup>
Carbon Monoxide		0.11	0.09 <sup>i</sup>	0.26			0.10	0.06 <sup>i</sup>	
Ethane		0.17	0.18 <sup>i</sup>				0.30	0.24 <sup>i</sup>	0.23 <sup>i</sup>
Ethylene		0.17	0.22 <sup>i</sup>				0.27	0.14 <sup>i</sup>	0.1
Acetylene		0.04						<0.02	
Water		0.81						0.5 <sup>i</sup>	
Formaldehyde		0.30						0.13 <sup>i</sup>	
Acetaldehyde		1.71		3.1 <sup>i</sup>		1.9	1.4	1.9 <sup>i</sup>	
Total Carbonyl		2.1	3.00 <sup>i</sup>						
2,3-Butanediol				1.7 <sup>i</sup>		1.3	2.0	2.2 <sup>i</sup>	
Total Vicinal Glycol		1.05	1.40 <sup>i</sup>					2.4	2.8
Reference	(64)	(17)	(30)	(43)	(44)	(47)	(23)	Present Work	(103)





TABLE IV-3 (Continued)

Conditions of Radiolysis

	a	b	c	d	e	f	g	h	i
Radiolytic Source	Co <sup>60</sup>	He <sup>++</sup>	He <sup>++</sup>	Co <sup>60</sup>	Co <sup>60</sup>	Pulsed electron	Co <sup>60</sup>	Co <sup>60</sup>	Co <sup>60</sup>
Dose Rate e.v./gm/hr.	0.8 x 10 <sup>18</sup>	3800 x 10 <sup>18</sup>	1300 x 10 <sup>18</sup>	0.1 x 10 <sup>18</sup>	0.4 x 10 <sup>18</sup>	13 150 x 10 <sup>18</sup>	13 150 x 10 <sup>18</sup>	1 - 60 x 10 <sup>18</sup>	2.2 x 10 <sup>18</sup>
Total Dose e.v./gm	5 x 10 <sup>20</sup>	75 x 10 <sup>20</sup>	3 - 300 x 10 <sup>20</sup>	0.2 - 1 x 10 <sup>18</sup>	4 - 15 x 10 <sup>18</sup>	0.1 - 1.5 x 10 <sup>20</sup>	0.1 - 1.5 x 10 <sup>20</sup>	*	10 <sup>18</sup> - 10 <sup>19</sup>

Remarks on Table IV-3

i: The superscript "i" denotes an initial yield as obtained from a product yield versus dose study.

Where initial G values are given, the dose range over which the results were obtained are given in the Total Dose row.

The numerical values listed in the Dose Rate row are approximate.

\* The lowest total dose for the values given in the "h" (Present Work) column are as follows:

Total Dose:	Major Gaseous Products	2 x 10 <sup>18</sup> e.v./gm.
	Major Liquid Products	1 - 10 x 10 <sup>19</sup> e.v./gm.
	Water	6 x 10 <sup>20</sup> e.v./gm.



### Unidentified Liquid Products from the Ethanol - 1,3-Pentadiene System

The suggestion that the diene acts as an energy or charge transfer agent as well as a radical scavenger is supported by the behaviour of some liquid products that arise from the ethanol-diene system (see Figure III-15 (B) and (C)). The maximum yield for two liquid products that arise in this system occurs in a diene concentration region that is an order of magnitude greater than that in which the glycol disappears completely. Since the aldehyde is not scavenged, if radical scavenging of the glycol and hydrogen formation reactions were the only inhibiting mode, then the maximum yield of a liquid "cross product" between ethanol and diene should appear at pentadiene concentrations where glycol is first completely inhibited ( $\epsilon_p = 0.004$ ). Thus, the liquid products that exhibit their maximum yield at 0.04 electron fraction pentadiene may arise solely from pentadiene rather than ethanol-pentadiene combination (or entities derived from them). The behaviour of these products is consistent with an energy or charge transfer mechanism between the diene and alcohol, i.e.



or







## (B) Gas Phase Radiolysis

### a) Comparison of $\gamma$ -Radiolysis of Ethanol in the Liquid and Gas Phases

The most obvious distinction between the results of the  $\gamma$  -radiolysis of liquid and gaseous ethanol is that in the liquid  $G(-\text{ethanol}) = 7.5$ , while in the gas phase  $G(-\text{ethanol}) = 13.9$ . Increased decomposition on going from the liquid to the gaseous phase has been observed in various systems<sup>(21), (24), (124), (125)</sup>. Part of the increase in the present system may be due to the higher temperature employed. However, methanol radiolysis in the two phases at room temperature showed more decomposition when the substrate was present as a vapor<sup>(24)</sup>.

If it is again postulated that the ratio  $\frac{G(\text{CH}_4)}{C(\text{H}_2)}$  indicates the ratio of C - C bond scission/(C - C + O - H) scissions the ratio is 0.31. Multiplying this ratio by 6 (the ratio of bonds involving hydrogen to C - C bonds in the molecule), the resultant ratio is 1.9. When compared to the analagous ratio of 0.7 for the liquid phase, it is evident that cage effects must be considered in the radiolysis of the liquid. The lack of cage effect in the gaseous phase, when considered with the much larger probability that ion-pairs escape immediate recombination in the gas phase, can account for a large part, if not all, of the enhanced decomposition of the alcohol in the gas phase. Moreover, an excited molecule would have less chance of becoming deactivated in the vapor state through collisions and hence the energetic entity would have a greater opportunity to generate observable stable products.





The nearly two fold increase in the extent of decomposition is reflected to varying degrees in each of the observed products, all of which showed a greater yield in the gas phase, except in the cases of ethane and propane, where the yields are nearly the same in the two phases.

Water was not measured in the gas phase, but assuming a  $G(H_2O) = G(C_2 \text{ or greater hydrocarbon})$ , the empirical formula based on a mass balance analysis was  $C_{2.00} H_{6.15} O_{0.97}$ . This formula reflects the fact that  $\approx 0.5$  G units of hydrogen deficient products are unaccounted for; however, as no analysis for methanol, formaldehyde and minor glycol products was effected, the formula is reasonable.

Hydrogen bonding may also dictate, to some extent, the degree of decomposition in the liquid phase. This type of bonding would be absent in the vapor state.

Some salient features of the gas phase radiolysis, compared to similar liquid phase experiments are outlined below.

#### Products Volatile at $-196^\circ C$ .

Most of the hydrogen arising in the gas phase ( $G = 7.5$  at a dose of  $4 \times 10^{20}$  e.v./gm) is inhibited by the addition of 0.2 electron fraction of 1,3-pentadiene. The ratios of  $\frac{G(H_2) \text{ inhibited liquid}}{G(H_2) \text{ inhibited gas}}$  and  $\frac{G(H_2) \text{ pure liquid}}{G(H_2) \text{ pure gas}}$  are both 0.6.

There is a 4 fold increase in  $G(\text{methane})$  on going from the liquid to the vapor state. Approximately 90% of this yield can be

The first part of the paper discusses the importance of maintaining accurate records of all transactions. It is essential for the company to have a clear and concise system in place to ensure that all data is properly recorded and stored. This will allow for easy access and retrieval of information when needed.

The second part of the paper focuses on the importance of regular communication and collaboration between all team members. It is crucial for everyone to stay informed about the company's goals and objectives, as well as the progress of various projects. Regular meetings and updates will help to ensure that everyone is working towards the same goals and that any issues are identified and resolved promptly.

The third part of the paper discusses the importance of maintaining a high level of security for all company data. This includes implementing strong password policies, using secure communication channels, and regularly updating software and systems to protect against potential threats. It is also important to ensure that all employees are trained on proper security protocols and are aware of the risks associated with data breaches.

The fourth part of the paper focuses on the importance of maintaining a high level of customer satisfaction. This involves providing excellent customer service, responding to inquiries promptly, and ensuring that all products and services meet the highest quality standards. Regular feedback from customers can help to identify areas for improvement and ensure that the company is always meeting the needs of its clients.

The fifth part of the paper discusses the importance of maintaining a high level of financial transparency. This involves providing regular updates on the company's financial status, including income, expenses, and profits. It is also important to ensure that all financial transactions are properly recorded and audited to prevent any fraud or mismanagement of funds.

The sixth part of the paper focuses on the importance of maintaining a high level of employee satisfaction and engagement. This involves providing a supportive work environment, offering opportunities for professional growth and development, and ensuring that all employees are treated fairly and with respect. Regular communication and feedback from employees can help to identify areas for improvement and ensure that the company is always providing a positive work experience for all its staff.

The seventh part of the paper discusses the importance of maintaining a high level of environmental sustainability. This involves implementing eco-friendly practices, such as reducing paper usage, recycling, and using energy-efficient lighting and equipment. It is also important to ensure that all company activities are in compliance with local and international environmental regulations.

The eighth part of the paper focuses on the importance of maintaining a high level of social responsibility. This involves supporting local communities, donating to charitable organizations, and ensuring that all company activities are in line with ethical principles. Regular communication and reporting on social responsibility efforts can help to build trust and credibility with the public and other stakeholders.

The ninth part of the paper discusses the importance of maintaining a high level of innovation and creativity. This involves encouraging all employees to think outside the box and come up with new ideas and solutions. It is also important to provide the resources and support needed to develop and implement these ideas, as well as to reward and recognize employees for their contributions.

The tenth part of the paper focuses on the importance of maintaining a high level of overall company performance. This involves setting clear goals and objectives, monitoring progress regularly, and making adjustments as needed. It is also important to ensure that all company activities are in line with the overall mission and vision of the organization, and that all employees are working towards the same goals and objectives.

inhibited by diene at  $\epsilon_p = 0.2$ . As almost all of the methane is scavengeable, this is support for the idea that most of the methane in the gas phase has a methyl radical precursor.

$G(\text{carbon monoxide})$  is approximately 10 fold greater in the vapor than in the liquid state radiolysis. It was shown that 1,3-pentadiene has no effect upon carbon monoxide formation in the liquid phase. If the same were true in the vapor state, at  $\epsilon_p = 0.2$ ,  $\frac{G(\text{CO}) \text{ inhibited}}{G(\text{CO}) \text{ pure}}$  would be 0.8. The last column of Table III-31 shows the observed ratio is 0.5. Therefore, there is some inhibition of CO in the gas phase. The effect, however, is considerably less than that for hydrogen or methane.

#### Products Volatile at $-112^\circ \text{C}$ .

Table III-32 shows that  $G(\text{ethane})$  is about the same in both phases. Pentadiene appears to inhibit ethane formation more effectively in the gas than in the liquid phase.

Table III-32 also demonstrates that  $\frac{G(\text{ethylene}) \text{ gas phase}}{G(\text{ethylene}) \text{ liquid phase}} \approx 10$ .

If there were no inhibition of this product by pentadiene, the expected G value would be  $G(\text{ethylene})$ , for pure alcohol  $\times 0.80$

$$= 1.15 \times 0.80$$

$$= 0.92 .$$

This calculated value agrees well with that actually observed (0.88) and it thus appears that this product is not appreciably affected by

The first part of the paper is devoted to a discussion of the  
general principles of the theory of the structure of the  
crystal lattice. It is shown that the structure of the  
crystal lattice is determined by the arrangement of the  
atoms in space. The arrangement of the atoms is  
determined by the forces of attraction and repulsion  
between them. The forces of attraction are due to the  
electrostatic interaction between the positive and  
negative ions. The forces of repulsion are due to the  
Pauli exclusion principle. The balance of these forces  
determines the equilibrium distance between the  
atoms. The equilibrium distance is the distance at  
which the forces of attraction and repulsion are in  
balance. The equilibrium distance is the distance at  
which the potential energy is a minimum. The  
equilibrium distance is the distance at which the  
crystal lattice is most stable. The equilibrium  
distance is the distance at which the crystal lattice  
has the lowest energy. The equilibrium distance is  
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properties of the crystal lattice. It is shown that the  
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equilibrium distance is the distance at which the  
potential energy is a minimum. The equilibrium distance  
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diene in the vapor phase. Therefore, the mechanism in this phase may be the same as that proposed for the liquid, i. e.

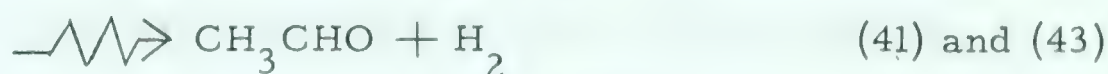
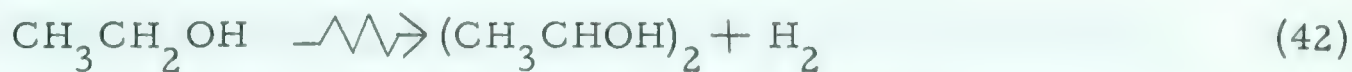


The ten fold increase would be due to the  $\text{CH}_3\text{CH}_2\text{OH}^*$  species having more opportunity to decompose before being deactivated by collisions with surrounding molecules.

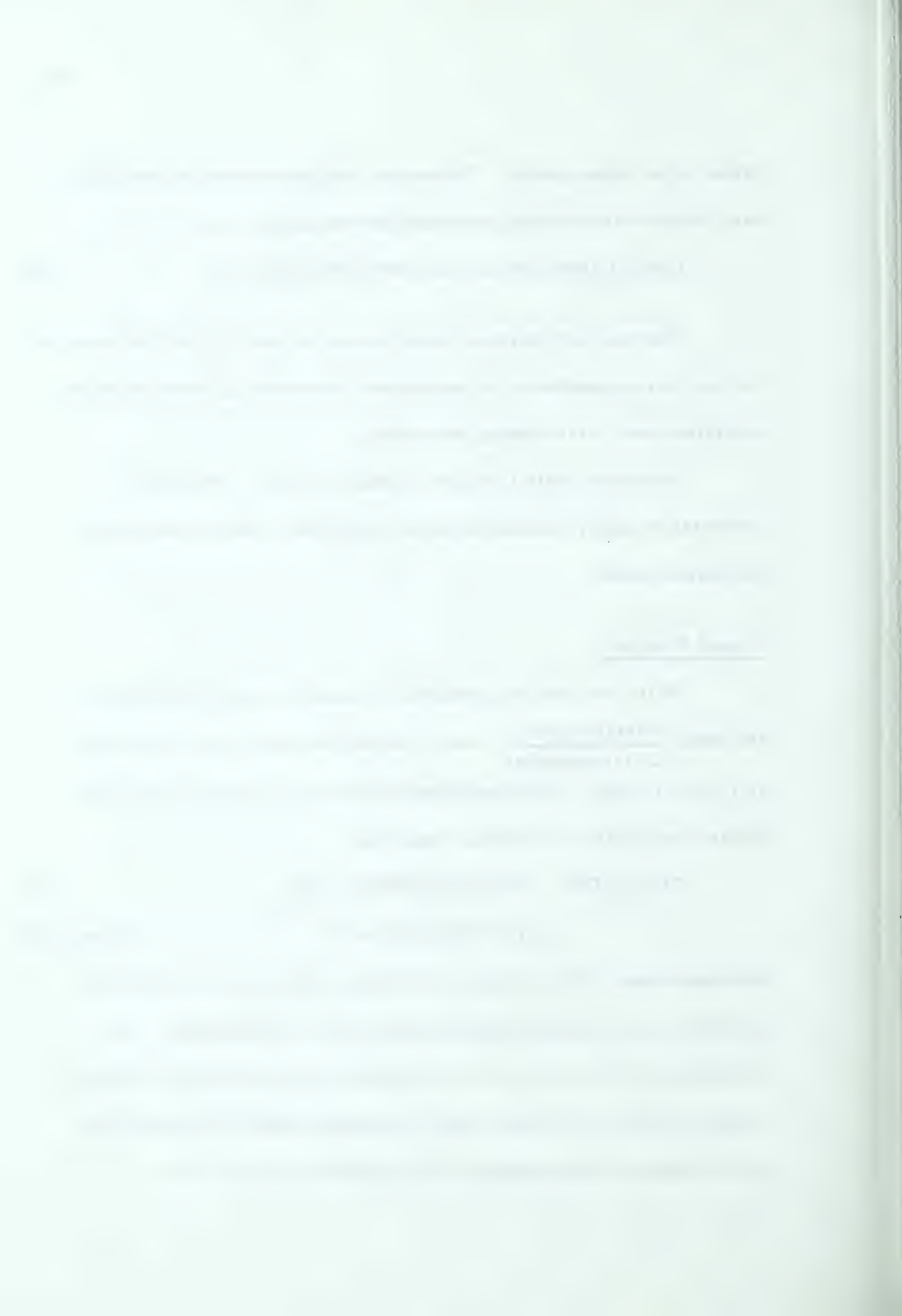
Acetylene yield is higher in the gas phase, which fact indicates a larger concentration of  $\text{C}_2\text{H}_4^*$  than that prevailing in the liquid phase.

### Liquid Products

While both major products increased in yield, the value of the ratio  $\frac{\text{acetaldehyde}}{\text{2,3-butanediol}}$  was 0.86 for the liquid and it increased to 1.13 in the gas. Both compounds are major products in the two phases and so the two overall reactions



are important in both phases. In the gas, the glycol is completely inhibited at an electron fraction of 0.20 of 1,3-pentadiene. The acetaldehyde (in contrast to its behaviour in the liquid) is inhibited from 3.5 to 1.4; the latter yield is approximately the same value as in ethanol-1,3-pentadiene liquid samples at  $\epsilon_p = 0.2$ .



The complete inhibition of 2,3-butanediol makes it appear that reaction (52)



is the glycol forming reaction in the gas as well as the liquid phase.

The greater amount of aldehyde in the gas phase (mostly inhibitable) is possibly due to enhancement of reactions (53) to (55). The unscavenegable aldehyde is the same in both phases and so reaction (47) probably occurs to the same extent in the liquid and gas phase radiolysis.

### 1,2-Propanediol

As this product is formed from the combination of  $\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CHOH}$ , the 7-fold increase in its yield on going from the liquid to the gas phase again illustrates the enhanced C - C bond breakage in the vapor state.

### b) Comparison of $\gamma$ - and $\alpha$ - Gas Phase Radiolysis of Ethanol

Table IV-4 shows the present gas phase yields obtained from  $\text{Co}^{60}$   $\gamma$ -radiolysis and those from a  $\text{Po}^{210}$   $\alpha$ - gas phase radiolysis study<sup>(21)</sup>.  $G(\text{H}_2)$  is very nearly the same in both cases. The most striking difference between the two sets of results is the acetaldehyde/2,3-butanediol ratio; the ratio = 1.1 for  $\gamma$ 's and 3.8 for  $\alpha$ 's. The conditions, pressure, temperature, etc., in the two studies were similar and could not account for the widely different ratios. Although no (or at least a greatly reduced) LET



TABLE IV-4

Product Yields from the Gas Phase Radiolysis of Ethanol

Product	G(Product) Present Work	G(Product) Reference (21)
Hydrogen	7.5	7.6
Methane	2.3	1.7
Carbon Monoxide	0.6	1.1
Ethane	0.2	0.2
Ethylene	1.2	0.7
Acetylene	0.09	0.03
Propane	0.01	
Acetaldehyde	3.5	4.5
2,3-Butanediol	3.1	1.2
1,2-Propanediol	0.9	0.15
Radiolytic Agent	$\text{Co}^{60} \gamma$ Rays	$\text{Po}^{210} \alpha$ -particles
Approximate dose (e.v./gm)	$4 \times 10^{20}$	$6 \times 10^{20}$
Irradiation Temperature	$105 \pm 3^\circ \text{C.}$	$108^\circ \text{C.}$



# Table 1

Table 1: Summary of the data collected during the experiment.

Time (s)	Distance (m)	Speed (m/s)
0.0	0.0	0.0
0.5	0.5	1.0
1.0	1.0	2.0
1.5	1.5	3.0
2.0	2.0	4.0
2.5	2.5	5.0
3.0	3.0	6.0
3.5	3.5	7.0
4.0	4.0	8.0
4.5	4.5	9.0
5.0	5.0	10.0
5.5	5.5	11.0
6.0	6.0	12.0
6.5	6.5	13.0
7.0	7.0	14.0
7.5	7.5	15.0
8.0	8.0	16.0
8.5	8.5	17.0
9.0	9.0	18.0
9.5	9.5	19.0
10.0	10.0	20.0
10.5	10.5	21.0
11.0	11.0	22.0
11.5	11.5	23.0
12.0	12.0	24.0
12.5	12.5	25.0
13.0	13.0	26.0
13.5	13.5	27.0
14.0	14.0	28.0
14.5	14.5	29.0
15.0	15.0	30.0
15.5	15.5	31.0
16.0	16.0	32.0
16.5	16.5	33.0
17.0	17.0	34.0
17.5	17.5	35.0
18.0	18.0	36.0
18.5	18.5	37.0
19.0	19.0	38.0
19.5	19.5	39.0
20.0	20.0	40.0
20.5	20.5	41.0
21.0	21.0	42.0
21.5	21.5	43.0
22.0	22.0	44.0
22.5	22.5	45.0
23.0	23.0	46.0
23.5	23.5	47.0
24.0	24.0	48.0
24.5	24.5	49.0
25.0	25.0	50.0
25.5	25.5	51.0
26.0	26.0	52.0
26.5	26.5	53.0
27.0	27.0	54.0
27.5	27.5	55.0
28.0	28.0	56.0
28.5	28.5	57.0
29.0	29.0	58.0
29.5	29.5	59.0
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32.5	32.5	65.0
33.0	33.0	66.0
33.5	33.5	67.0
34.0	34.0	68.0
34.5	34.5	69.0
35.0	35.0	70.0
35.5	35.5	71.0
36.0	36.0	72.0
36.5	36.5	73.0
37.0	37.0	74.0
37.5	37.5	75.0
38.0	38.0	76.0
38.5	38.5	77.0
39.0	39.0	78.0
39.5	39.5	79.0
40.0	40.0	80.0
40.5	40.5	81.0
41.0	41.0	82.0
41.5	41.5	83.0
42.0	42.0	84.0
42.5	42.5	85.0
43.0	43.0	86.0
43.5	43.5	87.0
44.0	44.0	88.0
44.5	44.5	89.0
45.0	45.0	90.0
45.5	45.5	91.0
46.0	46.0	92.0
46.5	46.5	93.0
47.0	47.0	94.0
47.5	47.5	95.0
48.0	48.0	96.0
48.5	48.5	97.0
49.0	49.0	98.0
49.5	49.5	99.0
50.0	50.0	100.0

effect would be expected in the gas phase, the nature of the radiolytic agent appears to be the only factor that can account for the difference in the relative amounts of the liquid products. The same trend was noted in a comparative study of  $\gamma$  's and  $\alpha$  's in liquid methanol, where LET effects would certainly be operative.

Although agreement between the minor product yields is not good, most G values are comparable, except in the case of 1,2-propanediol. Paralleling the higher yield of 2,3-butanediol for  $\gamma$  -radiolysis, a much higher propanediol yield was also observed for  $\gamma$  -radiolysis.

#### c) Radiolysis Mechanism in the Gas Phase

In the gas phase ionization events leading to stable products would be more favorable than in the condensed phases, as the electron can more easily escape from the parent ion. There have been numerous attempts to correlate mass spectral and radiolytic data<sup>(13), (18), (64), (126), (127)</sup>, especially for gas phase radiolysis. Decomposition mechanisms for radiolysis gaseous methanol based on mass spectral data have been proposed<sup>(24), (39), (128)</sup>.

Mass spectrometric analysis employing electron bombardment<sup>(129)</sup> of ethanol showed that the most abundant ion (43% of the total ionization) is due to the C - C split in the molecule; this is in accord with the high yield of methane found in the gas phase. The next most abundant ion is due to loss of a hydrogen atom which

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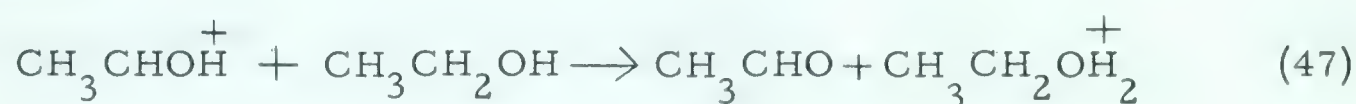
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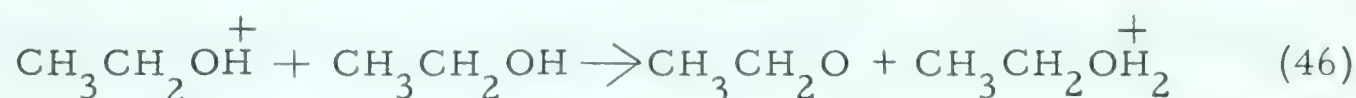
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arises mostly from the methylene position. This fact was proven by results of  $\text{CH}_3\text{CD}_2\text{OH}$  mass spectrometric analysis.

As acetaldehyde can be inhibited to the value of 1.4 in the gas phase it is assumed that reaction (47) occurs to this extent in the gas phase.



Due to the lack of hydrogen bonding it is unlikely that reaction (46) occurs to an appreciable degree.



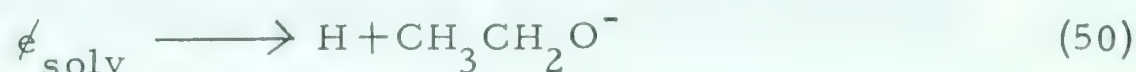
As the yield of scavengeable acetaldehyde is large ( $G \approx 2$ ) reactions (53-55) are important in the gas phase. The ethoxy radicals required for these reactions may be generated by



To be consistent with the approximate aldehyde to glycol ratio of 1 there must be three times as much  $\alpha$ -radicals as ethoxy radicals. (This assumes reaction (55) is not important.)



In the gas phase two other reactions, both involving negative ions, will be considered to be unimportant,

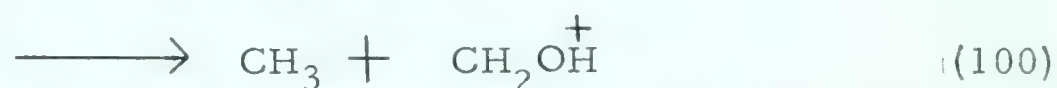
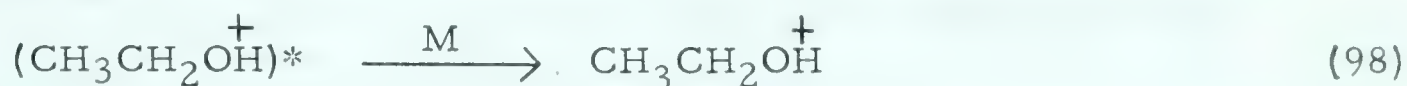


The mass spectrometric pattern for the breakdown of ethanol<sup>(128)</sup> indicates that methane would be a much more important product in the gas phase radiolysis, which it was. The apparent lack of ethoxy radicals in the mass spectrometric pattern makes it

The first part of the paper discusses the importance of the study and the objectives of the research. It also outlines the methodology used in the study and the results obtained. The second part of the paper discusses the implications of the study and the conclusions drawn from the research. It also outlines the limitations of the study and the areas for further research. The third part of the paper discusses the significance of the study and the contributions it makes to the field. It also outlines the practical applications of the study and the policy implications of the research. The fourth part of the paper discusses the future of the study and the areas for further research. It also outlines the challenges faced by the study and the opportunities for future research. The fifth part of the paper discusses the conclusion of the study and the final thoughts of the researcher. It also outlines the key findings of the study and the overall message of the research.



appear that processes involving excited molecules, or excited ions that give rise to hydrogen atoms and ethoxy radicals, also play a role in the radiolysis in the gas phase. The greater yields may be a reflection of the enhanced participation of the following type of reaction



The relatively large amounts of the  $\text{COH}^+$  ion found by mass spectrometry makes it appear likely that part of the 10 fold increase in carbon monoxide in the gas phase is due to this ion, which would generate carbon monoxide by loss of a proton.

In a study of charge exchange collisions of ethanol with positive ions in a mass spectrometer<sup>(130)</sup>, it was found that ions formed by loss of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  were of low intensity. This observation indicates that these products are formed from highly excited neutral molecules. Considering the formation of the neutral species by radiolysis, it is reasonable to assume they are also derived from highly energetic entities, which would arise in reactions of the type



which have been discussed previously for the liquid phase. In the gas phase, the occurrence of such excited molecule reactions would be greater, as the number of deactivating collisions before

The first part of the paper discusses the importance of the study and the objectives of the research. It also provides a brief overview of the methodology used in the study. The second part of the paper presents the results of the study and discusses the implications of the findings. The third part of the paper concludes the study and provides some final thoughts on the research.

The study was conducted using a qualitative research approach. The data was collected through interviews with participants who were selected through purposive sampling. The interviews were conducted in a semi-structured format, allowing the researcher to explore the topics in depth while also following a general guide. The data was then analyzed using thematic analysis, which involves identifying themes or patterns in the data.

The findings of the study suggest that there are several factors that influence the outcomes of the research. These factors include the quality of the data, the reliability of the participants, and the effectiveness of the research methods. The study also highlights the importance of careful planning and execution in conducting research.

In conclusion, the study provides valuable insights into the research process and the factors that influence its outcomes. It also emphasizes the need for ongoing research and improvement in the field.

decomposition would be less. It is, therefore, noteworthy that the yield of ethylene is increased 10-fold in the gas phase radiolysis, and the pentadiene (which acts primarily as a radical scavenger) does not inhibit the product in either phase.

However, most of the methane (90%) was inhibitable in the vapor state and so reaction (70) is not significant.

### C) Deuterated Ethanols

#### Hydrogen

Burr<sup>(18)</sup>, in his study of the  $\gamma$ -radiolysis of deuterated liquid ethanols, found different  $G(H_2)$  values than those reported here. However, the per cent deuterium contained by the radiolytic hydrogen is in fair agreement in both cases. The two sets of results are compared in Table IV-5. Both studies were carried out in the dose region where solvated electrons do not produce hydrogen (only hydrogen atoms and unscavengeable entities would contribute to  $G(H_2)$  ).

Burr explains his results by a scheme that involves initial production of hydrogen atoms from the methylene group, which is followed by abstraction from the hydroxyl group. The present mechanism requires that appreciable quantities of hydrogen atoms arise from the OH group, while abstraction is primarily from the  $\alpha$ -carbon atom. Lifshitz and Stein<sup>(66)</sup> also favor hydrogen atom production from the hydroxyl group.



TABLE IV-5

Percent Deuterium in the Radiolytic Hydrogen from Liquid Ethanols

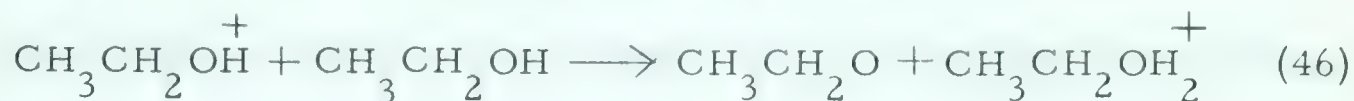
Alcohol	% Deuterium in Hydrogen	
	Present Work	Burr's Work (Reference 18)
$\text{CH}_3\text{CH}_2\text{OD}$	35.0	34.2
$\text{CH}_3\text{CD}_2\text{OH}$	40.8	42.0
$\text{CD}_3\text{CH}_2\text{OH}$	6.9	4.2
$\text{CD}_3\text{CD}_2\text{OH}$	54.2*	—
$\text{CD}_3\text{CD}_2\text{OD}$	97.0	93 - 95

\* Average of two determinations

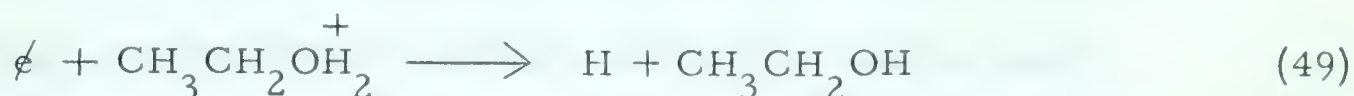




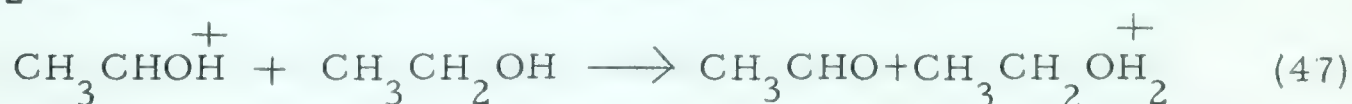
An ion-molecule reaction of ethanol (reaction 46) has been postulated in the mechanism for the liquid phase,



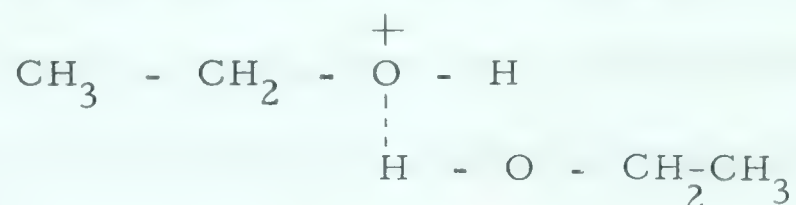
The ensuing reaction



is such that the hydroxyl position of the ethanol would be important for hydrogen formation. In low pressure gases it was found that the precursor to  $\text{CH}_3\text{CH}_2\text{OH}_2^+$  was  $\text{CH}_3\text{CHOH}^+$  rather than  $\text{CH}_3\text{CH}_2\text{OH}^+$ . For this reason reaction (47)



was postulated in the liquid. However, in the liquid state, reaction (46) would be facilitated by intermolecular hydrogen bonding, through formation of a transient state such as



Therefore reaction (46) is quite feasible in the liquid phase. In the gas phase, hydrogen bonding could not aid the formation of the above intermediate and it is assumed that reaction (46) is not important in the vapor. Support for this hypothesis can be derived from the deuterium results. All the OH alcohols showed a decrease in % H in the total hydrogen on going from the liquid to the gas. Furthermore  $\text{CH}_3\text{CH}_2\text{OD}$  showed a decrease in % deuterium in the total hydrogen in the gas phase. These facts can be accounted for by the decreased feasibility of the



above transition state due to lack of hydrogen bonding in the gas phase.

The large proportion (two thirds) of HD in the total hydrogen for both pure liquid  $\text{CH}_3\text{CH}_2\text{OD}$  and  $\text{CD}_3\text{CD}_2\text{OH}$  indicates that the hydroxyl group, and at least part of the ethyl group, are important for hydrogen formation, as is required in the liquid phase mechanism.

The per cent deuterium in the hydrogen from liquid  $\text{CD}_3\text{CH}_2\text{OH}$  is only 7%, which reflects on the fact that the methyl group is the least important of the three groups for hydrogen production. A large part of this 7% appears to arise from hydrogen arising in unscavengeable processes.

Quantitative estimation of the relative importance of the  $\text{CH}_2$  and OH positions is complicated by isotope effects. In the pure liquid there was 35% deuterium from  $\text{CH}_3\text{CH}_2\text{OD}$  and 45% light H from  $\text{CD}_3\text{CD}_2\text{OH}$ . The difference is due to the isotope substitution. As there was 41% deuterium from  $\text{CH}_3\text{CD}_2\text{OH}$  in the pure liquid the methylene group is the most important, the hydroxyl group is next, while the methyl group is relatively unimportant. This is what would be expected from the mechanism postulated at the beginning of the Discussion Section.

The same trend can be observed in the pure gas phase results but the methyl has doubled in importance (compared to the liquid) while the importance of the hydroxyl is less but still greater than that of the methyl group.

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Some measure of the complicating isotope effects can be obtained from the pure liquid results of  $\text{CD}_3\text{CD}_2\text{OD}$ . This alcohol was  $99.5 \pm 0.1\%$  isotopically pure at all positions. However, the radiolytic hydrogen contained 3% of the light isotope. If this is not due to mass spectrometric analysis error, it would reflect an overall isotopic effect of 6 for the ethanol molecule.

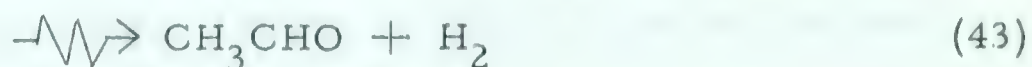
Molecular processes for hydrogen formation are discounted in Burr's interpretation. The benzene and 1,3-pentadiene results that were discussed previously, point out the occurrence of processes that need not necessarily be truly molecular in nature but are unscavengeable.

The liquid inhibited results again point the importance of the  $\text{CH}_2$  position, as the three alcohols that were deuterated in the  $\text{CD}_2$  position all showed lower  $G(\text{H}_2)$  total than the three alcohols that contained the  $\text{CH}_2$  group. ( $G(\text{H}_2) \text{ total} = G(\text{H}_2) + G(\text{HD}) + G(\text{D}_2)$ ). On going from light to perdeutero ethanol  $G(\text{H}_2)$  total decreases from 0.89 to 0.57.  $\text{CH}_3\text{CH}_2\text{OD}$  and  $\text{CD}_3\text{CH}_2\text{OH}$  give values of (0.86) and (0.82) which are close to that for the  $\text{CH}_3\text{CH}_2\text{OH}$ . For  $\text{CH}_3\text{CD}_2\text{OH}$  the  $G$  is 0.72, which fact points out that the methylene group is the most important for unscavengeable hydrogen production. Evidence for the methyl group's participation is the fact that, although  $G(\text{D}_2)$  decreases from 0.40 to 0.15 from the pure to the inhibited liquid, the  $\text{CD}_3\text{CH}_2\text{OH}$  alcohol was the only one that showed a greater per cent deuterium



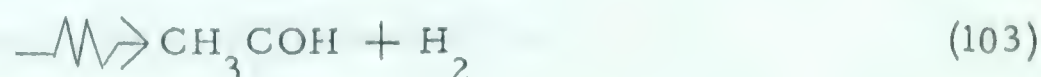
in the inhibited liquid compared to the pure. Both HD and D<sub>2</sub> increased in per cent of the observed total hydrogen. This alcohol showed the same behaviour in the gas phase where there was more unscavengeable hydrogen in all cases. The yield of total hydrogen for the inhibited samples in the gas phase also showed the importance of the alkyl group for unscavengeable hydrogen production. As in the liquid phase, the inhibited value of G(H<sub>2</sub>) total is smaller for the three CD<sub>2</sub> alcohols than for the three CH<sub>2</sub> alcohols, which points out the importance of the methylene position.

Unscavengeable hydrogen could arise from processes such as



If these reactions occurred to comparable extents the methylene position would be prominent as it is involved in both reactions.

The appreciable amounts of D<sub>2</sub> from inhibited CH<sub>3</sub>CD<sub>2</sub>OH and CD<sub>3</sub>CH<sub>2</sub>OH in the gas phase point out that processes such as



may occur to a limited extent.

### Methane

The results of Tables III-29 and III-30 indicate that the methyl radical that gives rise to methane abstracts from all positions, but mainly from the CH<sub>2</sub> and OH groups. The mixed

1. The first part of the paper is devoted to a general discussion of the problem.

2. The second part is devoted to a detailed analysis of the case of a single particle.

3. The third part is devoted to a detailed analysis of the case of a system of particles.

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methanes (i. e. methanes containing both H and D) that arise from  $\text{CH}_3\text{CH}_2\text{OD}$  and  $\text{CD}_3\text{CD}_2\text{OH}$  in the inhibited samples for both phases indicate that even in the unscavengeable methane the OH position plays a role.

### Ethylene

For all alcohols the ratio of ethylene in which a hydrogen atom appeared to have migrated in the ethanol molecule to "normal" ethylene is always greater in the gas phase.

### D) Suggestions for Future Work

At low doses ( $< 1 \times 10^{18}$  e.v./gm.) acetaldehyde may be scavengeable from its high value,  $\approx 3$ , to that observed at doses  $> 1 \times 10^{20}$  ( $G = 1.9$ ). Inhibitor studies in the low dose region may indicate the validity of reaction (53)



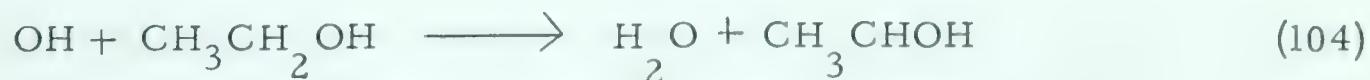
which may be inhibited by 1,3-pentadiene.

The mechanism for the formation of water could be elucidated by scavenger studies employing careful technique.

That is, if water arose from a process such as



followed by



$G(\text{H}_2\text{O})$  should be inhibited by an efficient scavenger for OH radicals.





A pressure dependence study of ethanol in the gas phase would indicate any product distribution or absolute yield changes as the ethanol changes from the nearly condensed phase to diffuse systems. Similarly, the  $\gamma$  -radiolysis of liquid ethanol at 105° C, (the temperature at which the gas phase runs were carried out) would indicate to what extent the increased temperature caused the increased decomposition.

Another type of investigation that might benefit the understanding of the mechanism of ethanol radiolysis would be the allied study of ethyl mercaptan. Oxygen and sulphur are in the same group of the periodic table; any large differences in the overall features of the radiolyses would result from the influence of the sulphur atom compared to the oxygen atom on the groups attached to it. That is, effects such as greatly decreased hydrogen bonding in the mercaptan could alter the overall radiolysis.



# REFERENCES

- 1) H. Fröhlich and R. L. Platzman, Phys. Rev. 92, 1152 (1953).
- 2) J. L. Magee, J. A. C. S. 73, 3270 (1951).
- 3) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry", John Wiley & Sons, New York (1964).
- 4) Handbook of Physics, Condon & Odishaw, McGraw-Hill Co., New York (1958).
- 5) R. L. Platzman, Rad. Res. 2, 1, (1955).
- 6) M. Burton, Record of Chem. Progress 19, 13 (1958).
- 7) P. Morrison, in Symposium on Radiobiology (at Oberlin College) 1950. Edited by J. J. Nickson
- 8) M. Burton, W. H. Hamill and J. L. Magee, United Nations Peaceful Uses of Atomic Energy - Proceedings of the Second International Conference - Geneva. Sept. 1958, Vol. 29, 391, (1958).
- 9) A. J. Swallow, "Radiation Chemistry of Organic Compounds" Pergamon Press, Oxford (1960).
- 10) M. Burton, J. of Chem. Education 36, 273 (1959).
- 11) J. L. Magee, Ann. Rev. of Nuclear Science 3, 171 (1953).
- 12) S. Dainton, Rad. Res. Supplement 1, 1 (1959).
- 13) J. G. Burr, J. Phys. Chem. 61, 1483 (1957).
- 14) A. S. Newton, J. Phys. Chem. 61, 1485 (1957).
- 15) H. A. Dewhurst, J. Phys. Chem 61, 1466 (1957).
- 16) P. Ausloos and J. F. Paulson, J. A. C. S., 80, 5117 (1958).
- 17) W. R. McDonell and A. S. Newton, J. A. C. S. 76, 4651 (1954).
- 18) J. G. Burr, J. A. C. S. 79, 751 (1957).
- 19) E. J. Hart, J. of Chem. Ed. 36, 266 (1959).





- 20) W. R. McDonell and S. Gordon, J. Chem. Phys. 23, 208 (1955).
- 21) J. M. Ramaradhya and G. R. Freeman, Can. J. of Chem. 39, 1836 (1961).
- 22) J. F. Franck and E. Rabinowitch, Trans. Faraday Soc. 30, 120 (1934).
- 23) R. H. Johnsen, J. Phys. Chem. 65, 2144 (1961).
- 24) J. H. Baxendale and R. D. Sedgwick, Trans. Faraday Soc. 57, 2157 (1961).
- 25) G. E. Adams and J. H. Baxendale, J. A. C. S. 80, 4215 (1958).
- 26) J. T. Allan, E. M. Hayon and J. Weiss, J. of Chem. Soc. 3913 (1959).
- 27) H. Zeldes and R. Livingstone, J. Chem. Phys. 30, 40 (1959).
- 28) A. Charlesby, "Atomic Radiation and Polymers", Pergamon Press, London (1960).
- 29) N. N. Lichtin, J. Phys. Chem. 63, 1449 (1959).
- 30) A. S. Newton and W. R. McDonell, J. A. C. S. 78, 4554 (1956).
- 31) T. O. Jones, R. H. Luebke, Jr., J. R. Wilson and J. E. Willard, J. Phys. Chem. 62, 9 (1958).
- 32) T. F. Williams, Trans. Faraday Soc. 57, 755 (1961).
- 33) T. F. Williams, Nature 194, 348 (1962).
- 34) C. S. Cummings and W. Bleakney, Phys. Rev. 58, 787 (1940).
- 35) F. W. Lampe, J. L. Franklin and F. H. Field, in "Progress in Reaction Kinetics", Vol. 1, edited by G. Porter, Pergamon Press (1961).
- 36) D. P. Stevenson and D. O. Schlissler, J. Chem. Phys. 23, 1353 (1955).
- 37) D. O. Schlissler and D. P. Stevenson, J. Chem. Phys. 24, 926 (1956).
- 38) D. P. Stevenson, J. Phys. Chem. 61, 1453 (1957).



- 39) P. Wilmenius and E. Lindholm, Arkiv för Fysik, Band 21, nr. 10, p. 97.
- 40) L. P. Theard and W. H. Hamill, J.A.C.S. 84, 1134 (1962).
- 41) P. Gray, Trans. Faraday Soc. 52, 344 (1956).
- 42) T. L. Cottrell, "The Strengths of Chemical Bonds", Butterworth's Scientific Publications, London (1958).
- 43) E. M. Hayon and J. Weiss, J. Chem. Soc., 3962 (1961).
- 44) G. E. Adams, J. H. Baxendale and R. D. Sedgwick, J. Phys. Chem. 63, 854 (1959).
- 45) J. W. Fletcher, Private communication.
- 46) J. M. Ramaradhyia and G. R. Freeman, Can. J. Chem. 39, 1843 (1961).
- 47) I. A. Taub and L. M. Dorfman, J.A.C.S. 84, 4053 (1962).
- 48) I. A. Taub, D. A. Harter, M. C. Sauer, Jr. and L. M. Dorfman, J. Chem. Phys. (to be published).
- 49) M. C. R. Symons and M. Townsend, J. Chem. Phys. 25, 1299 (1956).
- 50) R. S. Alger, T. H. Anderson and L. A. Webb, J. Chem. Phys. 30, 695 (1959).
- 51) R. H. Johnsen, J. Phys. Chem. 63, 2088 (1959).
- 52) R. H. Johnsen and D. A. Becker, J. Phys. Chem. 67, 831 (1963).
- 53) C. L. Luck and W. Gordy, J.A.C.S. 78, 3240 (1956).
- 54) R. Livingstone, J. of Chem. Ed. 36, 349 (1959).
- 55) M. Imamura, S. V. Choi and N. N. Lichtin, J.A.C.S., 85, 3565 (1963).
- 56) N. N. Lichtin, J. Phys. Chem. 63, 1449 (1959).
- 57) G. Mishitsuka and M. Burton, Rad. Res. 8, 285 (1958).
- 58) J. H. Baxendale and F. W. Mellows, J.A.C.S. 83, 4720 (1961).





- 59) L. M. Theard and M. Burton, J. Phys. Chem. 67, 59 (1963).
- 60) E. Hayon and J. Weiss, J. Chem. Soc. 3970 (1961).
- 61) B. Smaller and M. S. Matheson, J. Chem. Phys. 28, 1169 (1958).
- 62) G. E. Adams, J. H. Baxendale and J. W. Boag, Proc. Roy. Soc. (London), A277, 549 (1964).
- 63) I. A. Taub, M. C. Sauer, Jr. and L. M. Dorfman, Discuss. Faraday Soc. 36, 206 (1963).
- 64) J. G. Burr, J. Phys. Chem. 61, 1477 (1957).
- 65) J. G. Burr, J. Chem. Phys. 25, 587 (1956).
- 66) C. Lifshitz and G. Stein, J. Chem. Soc. 3706 (1962).
- 67) P. Riesz and B. E. Burr, Rad. Res. 16, 661 (1962).
- 68) Sr. P. J. Sullivan and W. S. Koski, J. A. C. S. 86, 159 (1964).
- 69) W. R. McDonell, J. Chem. Phys. 23, 208 (1955).
- 70) G. Mishitsuka, K. Ouchi, K. Hirota and G. Kusumoto, J. Chem. Soc., Japan 78, 129 (1957).
- 71) J. G. Burr, C. K. Dalton, R. A. Meyer, Abstracts of the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, 1960, p. 42-R, NAA-SR-5350.
- 72) M. K. Phibbs and B. de B. Darwent, J. Chem. Phys. 18, 495 (1950).
- 73) R. P. Porter and W. A. Noyes, Jr., J. A. C. S. 81, 2307 (1959).
- 74) R. F. Pottie, A. G. Harrison and F. P. Lossing, Can. J. Chem. 39, 102 (1961).
- 75) T. W. Shannon and A. G. Harrison, Can. J. Chem. 41, 2455 (1963).
- 76) M. Cher, J. of Phys. Chem. 67, 605 (1963).
- 77) A. R. Knight and H. E. Gunning, Can. J. of Chem. 39, 1231 (1961).





- 78) A. R. Knight and H. E. Gunning, Can. J. of Chem. 39, 2251 (1961).
- 79) A. R. Knight and H. E. Gunning, Can. J. of Chem. 39, 2466 (1961).
- 80) S. C. Lind and P. S. Rudolph, J. Chem. Phys. 26, 1768 (1957).
- 81) J. P. Mannion and M. Burton, J. Phys. Chem. 56, 560 (1952).
- 82) A. Singh and G. R. Freeman, (to be published).
- 83) L. F. Fieser, "Experiments in Organic Chemistry", 3rd edition, D. C. Heath and Co., Boston (1955).
- 84) F. Wild, "Characterization of Organic Compounds", 2nd edition, Cambridge University Press (1960).
- 85) Merck, Sharp and Dohme of Canada Ltd., personal communication.
- 86) D. N. Hume and W. E. Harris, Ind. Eng. Chem. Anal. Ed. 15, 465 (1956).
- 87) W. E. Harris, J. Chem. Ed. 35, 408 (1958).
- 88) T. P. Jones, Ph.D. Thesis, Chem. Dept., University of Alberta (1961), p. 49.
- 89) I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. II, Interscience Publishers (1952).
- 90) E. Eegrieve, Z. Anal. Chem. 110, 20 (1937); see "Formaldehyde" by J. F. Walker, Reinhold Publishing Corp., New York, 1944.
- 91) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds", 3rd edition, John Wiley and Sons Inc., New York, (1948).
- 92) Operation and Maintenance Manual for Gammacell 220, Atomic Energy of Canada Ltd., Ed. No. 2, June 1960.
- 93) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions", D. Van Nostrand Co. Inc., 1961.
- 94) E. J. Hart, W. J. Ramler and S. R. Rocklin, Rad. Res. 4, 378 (1956).



- 95) R. A. Sulit, E. J. Leahy and A. L. Baretti, "Principles of Radiation and Contamination Control" (1960), Navaships 250-341-3. Bureau of Ships, Navy Dept., Washington 25, D.C.
- 96) R. A. Back, T. W. Woodward and K. A. McLauchlan, Can. J. Chem. 40, 1380 (1962).
- 97) H. A. Bethe and J. Ashkin, in "Experimental Nuclear Physics" (ed. E. Segre) Vol. 1, John Wiley and Sons, New York (1953).
- 98) H. A. Bethe, "Handbuch der Physik", Julius Springer, Berlin, Vol. 24, 273 (1933); Ann. Physik 5, 325 (1930); Z. Physik 76, 293 (1932).
- 99) Prof. F. A. L. Anet (University of Ottawa), private communication, December, 1962.
- 100) R. H. Schuler, J. Phys. Chem. 60, 381 (1956).
- 101) I. B. Rabinovich, V. G. Golov, N. A. Efimova and S. M. Rustzmov, Academy of Sciences of the USSR Proceedings, Physical Chemistry Section 114, 339 (1957).
- 102) K. R. Ryan, L. W. Kieck, and J. H. Futrell, J. Chem. Phys. 41, 111 (1964).
- 103) G. E. Adams and R. D. Sedgwick, Trans. Faraday Soc. 60, 865 (1964).
- 104) P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne and W. H. Hamill, J.A.C.S., 84, 500 (1962).
- 105) M. R. Ronayne, J. P. Guarino and W. H. Hamill, J.A.C.S. 84, 4230 (1962).
- 106) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York (1940).
- 107) M. von Smoluchowski, Z. Phys. Chem. 92, 129 (1917).
- 108) J. J. J. Myron and G. R. Freeman, "The Radiolysis of Liquid Ethanol in the Presence and Absence of Benzene", Proceedings of the 2nd International Congress of Rad. Res., Harrogate, Great Britain, August, 1962.





- 109) A. Razbenbach and M. Szwarc , Proc. Royal Soc. A251, 394 (1959).
- 110) M. Levy and M. Szwarc, J. Chem. Phys. 22, 1621 (1954).
- 111) P. J. Dyne, J. Denhartog and D. R. Smith. Discus. Faraday Soc. 36, 135 (1963).
- 112) N. S. Hush and J. A. Pople, Trans. Faraday Soc. 51, 600 (1955).
- 113) K. Watanabe, T. Nakayama and J. Mottl, J. Quant. Spectros. Radiat. Transfer 2, 369 (1962).
- 114) C. N. R. Rao, "Ultra-Violet and Visible Spectroscopy: Chemical Applications," Butterworth's , London (1961).
- 115) G. S. Hammond, N. J. Turro, and P. A. Leersmaker, J. Phys. Chem. 66 1144 (1962).
- 116) S. Siggia, "Quantitative Organic Analysis via Functional Groups", John Wiley and Sons Inc., New York (1949).
- 117) J. H. Baxendale and F. W. Mellows, unpublished data (cited in reference 103).
- 118) S. J. Lapporte, Angew. Chem. 72, 759 (1960).
- 119) R. J. Cvetanovic, "Advances in Photochemistry", Vol. 1, edited by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers (John Wiley and Sons), New York (1963).
- 120) G. R. Freeman, Proc. Roy. Soc. A245, 75 (1958).
- 121) J. A. Barnard and H. W. D. Hughes, Trans. Faraday Soc. 56 , 55 (1960).
- 122) E. E. Royals, "Advanced Organic Chemistry", Prentice-Hall, Inc., N. J., (1958).
- 123) N. Bach, Proc. International Conf. Peaceful Uses of Atomic Energy, Geneva, Vol. VII, (1955).
- 124) R. F. Firestone, J. A. C. S., 79, 5593 (1957).

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- 125) J. M. Ramaradhya and G. R. Freeman, J. Chem. Phys. 34, 1726 (1961).
- 126) L. M. Dorfman and M. C. Sauer, Jr., J. Chem. Phys. 32, 1886 (1960).
- 127) J. H. Futrell, J. Chem. Phys. 35, 353 (1961).
- 128) E. Lindholm and P. Wilmenius, Arkiv för Kemi 20, 255 (1963).
- 129) L. Friedman, F. A. Long and M. Wolfsberg, J. Chem. Phys. 27, 613 (1957).
- 130) H. von Koch and E. Lindholm, Arkiv för Fysik 19, 123 (1961).









**B29827**